THE CALCULATION OF ELECTRONIC CHARGES IN MOLECULES USING A SIMPLIFIED SEMI-EMPIRICAL 'ATOMS IN MOLECULES' METHOD.

This thesis is submitted according to the requirements of the University of Warwick for the degree of Doctor of Philosophy.

The work described has not been submitted for any other degree or thesis.

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PREFACE

The work to which this thesis relates was carried out in the School of Molecular Sciences at the Univeristy of Warwick between January 1971 and May 1973.

I would like to gratefully acknowledge the help given to me by Dr. H. D. B. Jenkins who supervised this work.

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CONTENTS

ABSTRACT

This thesis describes an approach to the problem of computing electronic charge distributions in molecules.

The molecule is treated as a collection of atoms in assumed valence states. Sigma and pi electrons are separated from each other. The sigma electron distribution is computed using a valence state scheme the essence of which is a system of orbital charge equations, a unique equation for each type of bond. The form of orbital charge equation for a bond X - Y described by an M.O.

$$\Psi = c_i \phi_i + c_j \phi_j$$

where ϕ_i and ϕ_j are the bonding A.O.'s (usually hybrid) on X and Y respectively is

$$N(XY) = k_{YX} N_T^Y - k_{XY} N_T^X + I_{XY}$$

where N(XY) is the charge in orbital ϕ_i in the bond X - Y. k_{YX}, k_{XY}, I_{XY} are all parameters and N_T^X, N_T^Y are the total charges on X and Y excluding the charges in ϕ_i and ϕ_j.

The interaction of the sigma electrons with the pi electrons is described in two ways. In the first method the interaction occurs through charge dependent inductive parameters h_X in the expression

$$\alpha_X = \alpha_c + h_X \beta_{cc} .$$

The sigma electron calculation is linked to a H.M.O. calculation to form an iterative method, the iterative self-consistent charge method - I.S.C.C.M.

In the second approach a P.P.P. ($\sigma + \pi$) method is developed in

which the sigma distribution provides a potential framework for the pi electrons. The W_μ terms in the diagonal matrix elements of the P.P.P. method are interpreted as valence state ionisation potentials (V.S.I.P.'s) of the pi orbitals and are expressed as functions of the charge distribution , sigma and pi.

The advantages and disadvantages of the two approaches are discussed and the charges obtained using both methods are compared with other results in the literature.

CHAPTER 1

INTRODUCTORY SURVEY

Though it might be true that the theoretical solution of all the problems of chemical interest are implicit in quantum mechanics[1], finding means of obtaining those solutions is quite another matter. In the early days of quantum chemistry many interesting chemical problems involving small molecules were treated in a detailed mathematical manner. However, it was not long before it became apparent that the size and complexity of most chemical molecules would effectively inhibit large-scale ab initio calculations.

The question naturally presents itself ..... "By an appropriate choice of empirical parameters can we obtain better agreement with experimental properties than can be obtained with a non-empirical scheme bounded by the Hartree-Fock limit?"[2]. Or, as Lykos puts it, when referring to pi - electron molecules, "having some information about the theoretical structure of the pi-electron approximation and a tremendous amount of empirical information about the chemical and physical properties of pi-electron systems, can some useful middle ground be found between completely empirical calculations on the one hand, and ab initio calculations based on the underlying theoretical structure on the other?"[3].

Many theoreticians have decided that there is a "middle way", and the result has been a vast and growing body of semi-empirical work[4]. Some workers have seen the answer to the problem not so much in finding semi-empirical parameters but rather in reproducing other accurate methods with economy in effort and cost. Whitehead has pointed out that because a method is ab initio it does not mean to say its results are the correct ones[5].

Although ways of tackling the molecular problem may differ, most

theoreticians agree on the main features of the problem. It may be as well to summarise these:-

1. The differential equation that must be solved for any particular system of interest is

$$\mathcal{H}_{tot}\Psi = E\Psi \qquad (1.1)$$

which is the Schrödinger equation. The Born Oppenheimer approximation can then be assumed so removing terms involving nuclear kinetic energy and thus allowing us to treat the system as a number of electrons moving within a fixed nuclear framework[6].

2. The simplest way of getting a reasonably good description of the wave function is to use the Hartree-Fock method[7].
3. An exact solution to (1.1) has not been obtained for any molecules containing more than one electron.
4. Having more than one electron leads straight into the problem of electron correlation[8]. It is largely for this reason that the Hartree-Fock energy (the total electronic energy calculated from the Hartree-Fock wave function) always differs from the true energy. There may be other sources of error if approximations are involved.

In the most accurate theoretical methods, a choice has to be made as to the form and number of the basis orbitals. In the simple Hückel theory, on the other hand, though the basis orbitals are not described explicitly they are assumed to be of the p_z type, familiar to most chemists[9]. Such orbitals are frequently called chemical orbitals. Many other workers have also tried to retain close links with the generally accepted ideas of orbitals and bonding in use in chemistry[10]. Where, in accurate methods,

orbitals are required in explicit form, Slater orbitals or Slater type orbitals (S.T.O.s) are frequently used[11]. These are located on the atoms comprising the molecule, and have provided a picture of the shapes of orbitals commonly used in all branches of chemistry.

It was found, however, that the theoretical evaluation of certain integrals appearing in the calculation was made easier if Gaussian type orbitals (G.T.O.s) were used, rather than S.T.O.s[12]. Such a step, unfortunately, poses a number of problems. For example, Gaussians do not bear much resemblance to the orbitals with which most chemists are familiar, nor do they provide a suitable basis for the molecular wave function.[13] On the other hand groups of Gaussians can be chosen to resemble S.T.O.s of the more conventional approach[14]. Some recent methods allow the Gaussians to "float" over the molecule until positions corresponding to the optimised energy are found[15]. The trouble with this is that the orbitals may not be centred on the atoms at all! Clearly some of these methods lead us a long way from the usual ideas of chemistry and make the interpretive approach difficult.

Needless to say, irrespective of whether S.T.O.s or G.T.O.s are used, the evaluation of all the integrals appearing in the full treatment is both lengthy and complex. In view of the fact that the total molecular energy is certainly inaccurate, the idea of using the energy as a comparative, rather than an absolute quantity suggests itself[16]. This view tends to support the use of semi-empirical methods rather than full theoretical ("non-empirical") treatments. Semi-empirical parameters probably include implicitly correlation effects and other sources of error and this is quite likely the main reason for their success[17]. A well-known example of this concerns the evaluation of the carbon $2p_z$ - $2p_z$ one-centre two-electron repulsion integral $(\mu\mu|\mu\mu)$, or $\gamma_{\mu\mu}$. Theoretical evaluation of $\gamma_{\mu\mu}$ leads

to the value 16.93ev.[62], whereas the semi-empirical treatment of Pariser and Parr in which γ_{cc} is equated to $I_c - A_c$ (18) gives a value of 11.13 ev. It is generally found that the latter value helps towards a more adequate description of molecular properties.

Where possible the practice is to identify among the quantities appearing in the elements of the Hartree-Fock matrix those that can be related to atomic quantities, like ionisation potentials and certain two-electron properties such as bond energies. It is quite customary to use atomic valence-state ionisation potentials (V.S.I.P.s) in the diagonal matrix elements of many semi-empirical methods[19]. This latter approximation seems, to the author, to neglect the fact that we are not dealing with an isolated atom. For example, in the pi electron approximation, one would expect sigma electronic effects which occur in the molecular situation to alter the V.S.I.P. of the pi orbital. There is some evidence for this view. The calculated V.S.I.P. of carbon in the valence state C (tr tr trπ) is 11.16 ev, from Jaffe's formulae[20]. In the methyl radical, in which the carbon atom is in the same valence state, the value of 9.95 ev. has been obtained from experiment[21]. This seems to suggest the use of a V.S.I.P. of less than 11 ev in the diagonal elements. Some workers have gone even further and have reduced the V.S.I.P. below 9.6 ev[22].

If the use of atomic properties is thought undesirable, what other considerations can the choice of parameters be based upon? It is more or less a fact of life, as far as semi-empirical workers are concerned, that the same set of parameters will seldom reproduce more than two chemical properties. It is for this reason that semi-empirical methods tend to be developed and parameterised with a particular end in view, such as calculation of heats of formation[23,27], prediction of photoelectron spectra[24], absorption spectra[25], electron spin resonance[26]. Justification for

parameter choice follows from successful predictions of chemical properties for one or two model molecules, and subsequent successful correlations with experiment for other molecules. In the present state of the art, theoretical calculations are almost always used in conjunction with other chemical or physico-chemical methods. Ideally speaking the number of parameters should be small, and the number of successful predictions large. However, there is frequently a tendency to introduce more and more parameters to obtain agreement with experiment, with consequent loss in generality of method.

To a certain extent the difficulties of parameterisation has led many theoreticians back to ab initio methods, the computations being aided considerably by up to date, fast, computers. It is still fair to say, however, that only in the very recent past have even average sized molecules been investigated by these methods.

It seems clear that in many areas of chemistry and biological chemistry there is a great need for reliable semi-empirical methods which can deal with different types of molecules and which need neither an enormous number of parameters nor hours of computing time. The present work is directed towards achieving such an end.

CHAPTER 2

CHEMICAL STRUCTURE - THE LOCALISED TWO-ELECTRON BOND

The idea of a two electron bond resulting from the overlap of two atomic orbitals, one on each atom and each containing one electron, has had central importance in chemistry for many years. From many points of view it has been very convenient to retain this concept of the chemical bond, largely because of its pictorial simplicity and its ability to shed light on many problems of chemical structure. The conventional picture of delocalised pi electrons has led to an understanding of much of organic chemistry in an analogous manner.

Since the advent of quantum chemistry, theoreticians have sought to explain the structures of molecules in terms of more or less approximate solutions of the Schrödinger wave equation. The various physically meaningful quantities which come out are then compared with experiment and with ideas generally accepted by chemists as a whole. It is often found that theory and practice compare favourably.

Sometimes, the chemist's general concepts of bonds are used as good but approximate starting points for theoretical analyses. For example, in the saturated molecule methane, consisting of the 1s core of carbon atom and four C--H bonds, we could write an approximate wave function in the form[28]

$$\Psi = C(1,2)[CH]_1(3,4)[CH]_2(5,6)[CH]_3(7,8)[CH]_4(9,10) \qquad (2.1)$$

where the numbers in round parenthesis refer to electron pairs. The problems with this function are that it is not anti-symmetric with respect to electron interchange, as required by the Pauli principle, and does not take into account the indistinguishability of the electrons. A more accurate ground state wave function can be represented by a Slater determinant built up from orthonormal spin orbitals ϕ_i.[29]

$$\Psi = (N!)^{-1/2} \sum_{P} (-1)^{P} P\left\{\phi_1(1)\,\bar{\phi}_1(2) \ldots\ldots \phi_{N/2}(N-1)\,\bar{\phi}_{N/2}(N)\right\} \tag{2.2}$$

Applying the Self Consistent Field (S.C.F.) method to the Schrödinger equation (1.1) with a function of form (2.2) yields the well known Hartree-Fock equation

$$h^N \phi_i + \sum_j (2J_j - K_j)\phi_i = \sum_k c_{ki}\phi_k \tag{2.3}$$

where J_j and K_j are the Coulomb and exchange operators respectively

$$J_j \phi_i(1) = \left(\int \phi_j^2(2)\, 1/r_{12}\, d\tau_2\right)\phi_i(1) \tag{2.4}$$

$$K_j \phi_i(1) = \left(\int \phi_j(2)\phi_i(2)\, 1/r_{12}\, d\tau_2\right)\phi_j(1) \tag{2.5}$$

and indices i, j, k label the ϕ. Subjecting equation (2.3) to variational treatment, one obtains the secular equations

$$\sum_s c_{is}\left[f_{rs} - e_i S_{rs}\right] = 0 \quad (i = 1,2,\ldots\ldots,N) \tag{2.6}$$

where

$$f_{rs} = h_{rs} + \sum_{t,u} 2P_{tu}\left[\iint \chi_r(1)\chi_s(1)\, 1/r_{12}\, \chi_t(2)\chi_u(2)\, d\tau_1 d\tau_2 - \tfrac{1}{2}\iint \chi_r(1)\chi_t(1)\, 1/r_{12}\, \chi_s(2)\chi_u(2)\, d\tau_1 d\tau_2\right] \tag{2.6a}$$

and indices r, s, t, u label the atomic orbitals χ, which are the basis functions. h_{rs} is the one-electron part of the mat rix element, P_{tu} is an element of the charge and bond order mat rix. The solutions of the secular equations give the eigenvalues and eigenvectors of the Hartree-Fock operator. The total electronic energy is given by

$$E = 2\sum_i h_i + \sum_{i,j}\left[2J_{ij} - K_{ij}\right] \tag{2.7}$$

or in terms of atomic orbitals by

$$E = 2\sum_i \sum_r \sum_s c_{ir} c_{is} h_{rs} + \sum_i \sum_j \left(\sum_r \sum_s \sum_t \sum_u c_{ir} c_{is} c_{jt} c_{ju} \right.$$
$$\left. \times \left\{ 2\iint \chi_r(1)\chi_s(1) \tfrac{1}{r_{12}} \chi_t(2)\chi_u(2) d\tau_1 d\tau_2 - \iint \chi_r(1)\chi_t(1) \tfrac{1}{r_{12}} \chi_s(2)\chi_u(2) d\tau_1 d\tau_2 \right\} \right) \quad (2.8)$$

The secular equations (2.6) result from the pseudo one electron problem

$$f \phi_i = \epsilon_i \phi_i \quad (2.9)$$

which can be regarded as formally analogous to the independent particle problem. The operator, f, depends on all the electrons so that equation (2.3) can only be solved iteratively. An exact solution to the S.C.F. problem is not possible because the set of basis functions is not infinite and hence not a complete set[30].

Ruedenberg has pointed out that though the variation treatment determines the total molecular function, Ψ, the individual orbitals ϕ_i, are not completely determined[31]. One could define a new set of solution orbitals, ψ_k, obtained through some unitary transformation T

$$\psi_k = \sum_{i=1}^{N} \phi_i T_{ik} \quad (2.10)$$

The new determinantal function, Ψ', is related to the previous one in such a way that

$$\Psi' = \det | \psi_1(1) \bar{\psi}_1(2) \cdots\cdots \bar{\psi}_{N/2}(N) | \quad (2.11)$$

$$\Psi = \Psi' (\det T)^2 \quad (2.12)$$

and since for a unitary transformation det T = $\pm$ 1

$$\Psi = \Psi' \quad (2.13)$$

Therefore, within the wave function, Ψ, one can carry out arithmetic operations on the ϕ_i to arrive at another set of solution orbitals ψ_k.

Ruedenberg has shown the possibility of finding such unitary transformations that lead to sets of localised orbitals in a number of molecules[31, 32]. Since the functions ϕ_i are linear combinations of the basis functions, this means finding new linear combinations of basis orbitals. If these M.O.'s are such that they have greatest amplitudes at particular pairs of atoms, and small or zero amplitudes at all the other atoms, then the M.O.'s can be said to be localised over that pair. The suitability of such localised descriptions obviously depends on the smallness of the amplitude of the M.O. at all atoms except the two in question.

Let us consider methane as an example. The methane molecule belongs to the Td point group and the four hydrogen 1s orbitals form a basis for the irreducible representations A_1 and T_2

$$\begin{aligned} A_1 &\quad h_a + h_b + h_c + h_d \\ T_2 &\quad \begin{cases} h_a + h_b - h_c - h_d \\ h_a - h_b - h_c + h_d \\ h_a - h_b + h_c - h_d \end{cases} \end{aligned} \qquad (2.14)$$

where h_k stands for hydrogen 1s orbital. For the carbon atom, the carbon 2s orbital has the symmetry A_1, and the $2p_x$, $2p_y$ and $2p_z$ orbitals together have the symmetry T_2. Consequently we can form linear combinations of hydrogen and carbon orbitals of the same symmetry. This gives the delocalised M.O.'s

$$\begin{aligned} \psi_1 &= \alpha s + \beta (h_a + h_b + h_c + h_d) \\ \psi_2 &= \alpha' p_x + \beta' (h_a + h_b - h_c - h_d) \\ \psi_3 &= \alpha' p_y + \beta' (h_a - h_b - h_c + h_d) \\ \psi_4 &= \alpha' p_z + \beta' (h_a - h_b + h_c - h_d) \end{aligned} \qquad (2.15)$$

The ground state wave function for CH_4 is best represented by the Slater determinant

$$\Psi = 1/(8!)^{\frac{1}{2}} \det\{\psi_1(1)\bar{\psi}_1(2)\psi_2(3)\bar{\psi}_2(4)\psi_3(5)\bar{\psi}_3(6)\psi_4(7)\bar{\psi}_4(8)\} \quad (2.16)$$

By adding and subtracting rows and columns in this determinant one can obtain another determinant representing the ground state

$$\Psi' = 1/(8!)^{1/2} \det\{\psi_I(1)\bar{\psi}_I(2)\psi_{II}(3)\bar{\psi}_{II}(4)\psi_{III}(5)\bar{\psi}_{III}(6)\psi_{IV}(7)\bar{\psi}_{IV}(8)\} \quad (2.17)$$

where

$$\begin{aligned}
\psi_I &= 1/2\,(\psi_1 + \psi_2 + \psi_3 + \psi_4) \\
\psi_{II} &= 1/2\,(\psi_1 + \psi_2 - \psi_3 - \psi_4) \\
\psi_{III} &= 1/2\,(\psi_1 - \psi_2 - \psi_3 + \psi_4) \\
\psi_{IV} &= 1/2\,(\psi_1 - \psi_2 + \psi_3 - \psi_4)
\end{aligned} \quad (2.18)$$

The ψ_I etc are localised M.O.'s, the ψ_1 etc are delocalised M.O.'s.

In terms of atomic orbitals (A.O.'s) the localised M.O.'s are

$$\begin{aligned}
\psi_I &= 1/2\,[\alpha s + \alpha'(p_x + p_y + p_z) + (\gamma + 3\gamma')\tfrac{h_a}{4} + (\gamma - \gamma')(h_b + h_c + h_d)] \\
\psi_{II} &= 1/2\,[\alpha s + \alpha'(p_x - p_y - p_z) + (\gamma + 3\gamma')\tfrac{h_b}{4} + (\gamma - \gamma')(h_a + h_c + h_d)] \\
\psi_{III} &= 1/2\,[\alpha s + \alpha'(-p_x - p_y + p_z) + (\gamma + 3\gamma')\tfrac{h_c}{4} + (\gamma - \gamma')(h_a + h_b + h_d)] \\
\psi_{IV} &= 1/2\,[\alpha s + \alpha'(-p_x + p_y - p_z) + (\gamma + 3\gamma')\tfrac{h_d}{4} + (\gamma - \gamma')(h_a + h_b + h_c)]
\end{aligned} \quad (2.19)$$

or, in general

$$\psi_K^{loc} = 1/2\{\alpha' t_k + (\alpha - \alpha')s + 4\gamma' h_K + (\gamma - \gamma')(h_a + h_b + h_c + h_d)\} \quad (2.20)$$

where K = I, II, III, IV and k = 1, 2, 3, 4 respectively, and

$$t_1 = (s + p_x + p_y + p_z)$$

$$t_2 = (s + p_x - p_y - p_z)$$

$$t_3 = (s - p_x - p_y + p_z)$$

$$t_4 = (s - p_x + p_y - p_z)$$

$$h_1 = h_a \text{ etc.} \qquad (2.21)$$

which are of the same form as given by Ruedenberg[32], and by Daudel[28]. The extent to which (2.19) are accurate localised orbitals depends on the difference $(\gamma - \gamma')$. If $\gamma = \gamma' = \frac{1}{4}$

$$\psi_I = 1/2\,[\alpha s + \alpha'(p_x + p_y + p_z) + h_a]$$
$$\psi_{II} = 1/2\,[\alpha s + \alpha'(p_x - p_y - p_z) + h_b]$$
$$\psi_{III} = 1/2\,[\alpha s - \alpha'(p_x - p_y + p_z) + h_c]$$
$$\psi_{IV} = 1/2\,[\alpha s - \alpha'(p_x + p_y - p_z) + h_d] \qquad (2.22)$$

In this situation the components of the M.O. which come from the carbon atom are called the familiar sp^3 hybrids. When a set of localised orbitals exactly equivalent to a set of delocalised orbitals can be obtained, the localised orbitals are said to be "equivalent orbitals". Usually the localisation scheme is not perfect[35].

In analysing wave functions for some small molecules Ruedenberg found approximately localised orbitals[31]. Peters has found localised sigma type orbitals in more complex molecules involving sigma and pi type A.O.'s[33, 34]. These studies support the thesis that some bonds, mainly those composed of sigma type orbitals can be satisfactorily described by localised M.O.'s.

The fact that individual M.O.'s can be subjected to unitary transformations without altering the molecular wave function confers flexibility on M.O. theory. Thus M.O.'s can be localised or delocalised - and the former may include lone pair and hybrid orbitals - or a combination of both[33, 34]. The M.O.'s themselves may be written in terms of A.O.'s (L.C.A.O. scheme)[36],

bond orbitals (L.C.B.O. scheme)[37], or valence orbitals (L.C.V.O. scheme)[38], or combinations of all three. The A.O.'s, B.O.'s and V.O.'s must all be referred to an orthonormal basis set.

Another approach to the question of localised orbitals is the "separated electron pair" theory of Parks and Parr[39, 40]. The theory is based on the assumption that electrons with the same spin tend to stay far apart while electrons with opposed spin may be found in the same small region of space, usually between the nuclei of the constituent atoms. The best separation is the one that minimises the total electronic energy.

The total electronic wave function for a saturated molecule is of the form

$$\Psi = [\phi_A(1,2)\,\phi_B(3,4)\,.....\,\phi_M(2n-1,\,2n)] \qquad (2.25)$$

where each ϕ_I is an anti-symmetric function of the space and spin co-ordinates of the two electrons, and the brackets denote the normalised partial antisymmetrisation operator. This wave function can be treated in a manner analogous to that of the usual Hartree-Fock theory. For example, the electronic energy is given by

$$E = \int \Psi H \Psi \, d\tau = \sum_I I_I + \sum_{I<J} (J_{IJ} - K_{IJ}) \qquad (2.26)$$

The energy of a particular bond, K, can be expressed as

$$E_K = \iint \phi_K(1,2)\, H_K(1,2)\, \phi_K(1,2)\, d\tau_1 d\tau_2 \qquad (2.27)$$

$H_K(1,2)$ is a two electron Hamiltonian, which is satisfactory from the point of view that the properties of electron pair bonds are two electron ones.

$$H_K(1,2) = [H_N(1) + G_{\Lambda-K}(1)] + [H_N(2) + G_{\Lambda-K}(2)] + (e^2/r_{12}) \qquad (2.28)$$

where the $G_{\Lambda-K}$ are the Coulomb - exchange operators involving the mutual interactions of the pair K with the other pairs. The orthonormal pair

functions are written

$$\phi_K(i,j) = 1/\sqrt{2}\,\phi_K(i)\phi_K(j)[\alpha(i)\beta(j) - \alpha(j)\beta(i)] \qquad (2.29)$$

All the ϕ_K (i, j) can then be combined into the determinantal form

$$\Psi = 1/[(2n)!]^{1/2} \sum_P (-1)^P P[\phi_1(1)\bar{\phi}_1(2) \cdots\cdots \bar{\phi}_N(2n)] \qquad (2.30)$$

where the one electron M.O.'s ϕ_1 ϕ_2 ..... ϕ_N are assumed to be mutually orthonormalised. One could approximate the ϕ_i as linear combinations of atomic orbitals as mentioned earlier in this chapter and arrive at the usual integrals over atomic orbitals, although Parks and Parr choose a different approach[39].

CHAPTER 3

THE CONCEPT OF ORBITAL CHARGE EQUATIONS AND THEIR APPLICATION TO MOLECULES

(i) Orbital Charge Equations - Theoretical Background.

It was found that for certain isolated bond types, like C-H and C-C, the charge in the orbital on either of the atoms involved in bond formation can be expressed as a linear function of the charges in the other orbitals of the atoms concerned.[41] We should mention that these charges (i.e. those in the bonding orbital used to obtain the function) were calculated by the use of valence state energies as cited by Hinze, Jaffe et al, and consequently involved the electronegativity equalisation principle.[42]

We are not, in the present discussion, going to be too concerned about the source of the charges, they could, in principle, be those calculated in a variety of theoretical methods, our concern is more with the utilisation of the scheme proposed and its limitations.

Jenkins[43] found that in the CH system, the charge, N(CH) in the tetrahedrally hybridised orbital on the carbon atom directly bonded to the 1s orbital on hydrogen varied with charge in the other orbitals on the carbon atom in the quadratic manner shown in figure 3.1. The variation of N(CH) with N_T^C the total remaining charge on the carbon atom is given analytically by the quadratic relation.

$$N(CH) = 0.0177\, N_T^{C2} - 0.4791\, N_T^C + 2.3086 \qquad (3.1)$$

In the author's M.Sc. thesis[44], it was shown how simple Hückel theory could be developed to show the charge in an orbital N(AB) taking part in the formation of bond A-B could be written in the form

$$N(AB) = \frac{I_B^V - I_A^V}{2m\beta_{AB}} + 1 \qquad (3.2)$$

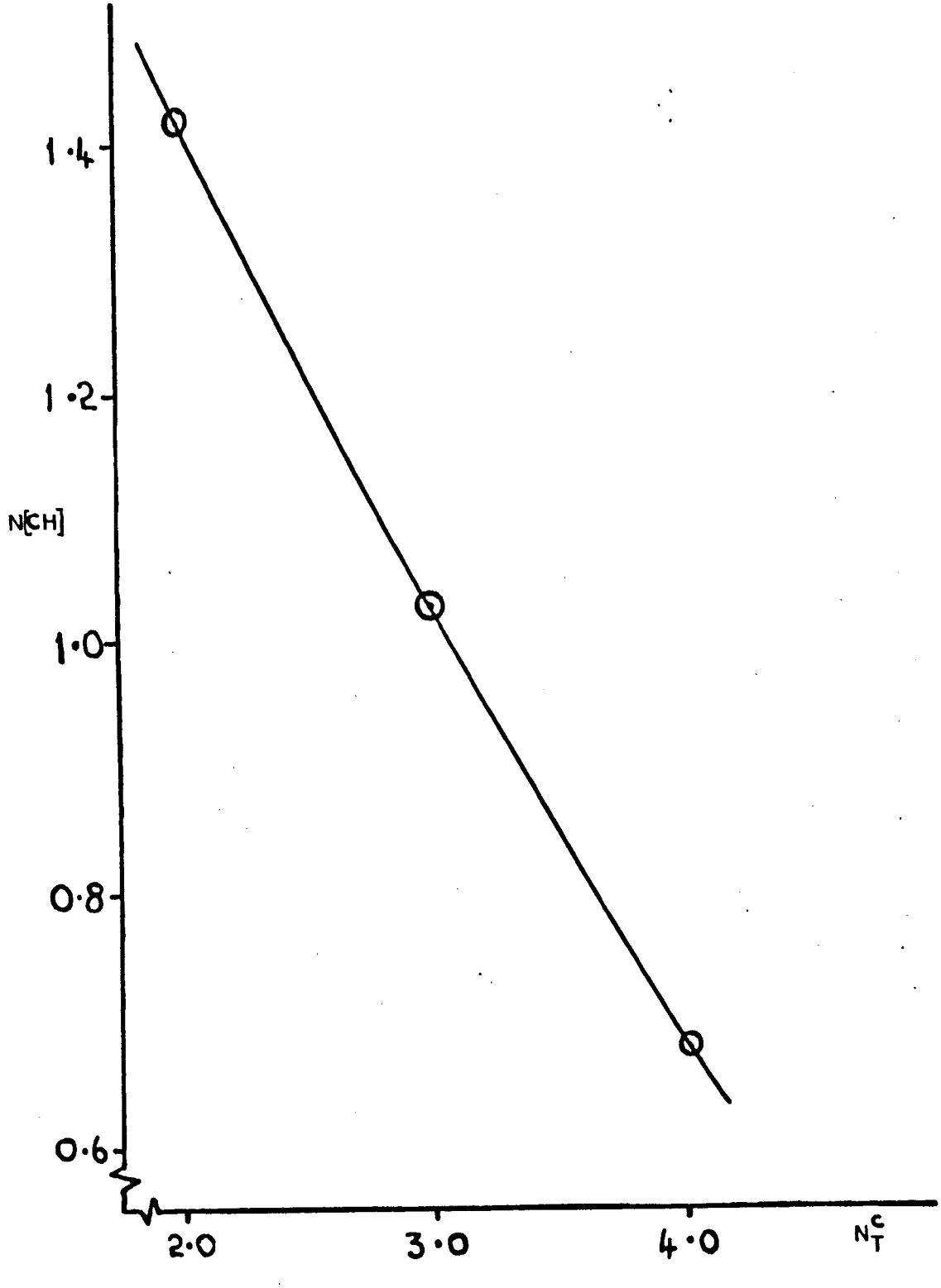


FIGURE 3.1. PLOT OF N[CH] VERSUS N_T^c.

where m is a constant, β_{AB} is a resonance integral and the I^V's are V.S.I.P.s. The equations of Hinze et al give V.S.I.P.s and V.S.E.A.s as quadratic functions of the charge in the other orbitals on the atoms involved in forming the bond. Equation (3·2) becomes

$$N(AB) = \frac{(A' + B'N_T^B + C'N_T^{B2}) - (A + BN_T^A + CN_T^{A2}) + 1}{2m\ \beta_{AB}} \qquad (3·3)$$

If atom B is univalent then we have

$$N(AB) = \frac{A'' - (A + BN_T^A + CN_T^{A2}) + 1}{2m\ \beta_{AB}} \qquad (3·4)$$

In the case of carbon, and many other atoms, coefficients C and C′ in equations (3·3) and (3·4) are much the smallest by at least an order of magnitude. Moreover, all the quantities in the denominator of (3·3) and (3·4) are greater than unity so that the quadratic terms are expected to be very small. The justification of this argument is borne out by the curve in figure one, where the slope is almost linear. We might expect the linear function to behave in a similar manner as the quadratic one in the regions of N_T^C of interest in most systems. Further justification for this expectation arises when we consider that bonds like C-H and C-C are only slightly polar, so that $N(CH) \simeq 1$, $N(CC) \simeq 1$ in most molecules and we need only consider values of N(CH) in the region $0·7 \leq N(CH) \leq 1·3$, a region in which the quadratic can be replaced by the tangent to the curve at the point $N_T^C = 3$, with little loss in accuracy. The orbital charge equation then becomes

$$N(CH) = -0·3729\ N_T^C + 2·1493 \qquad (3·5)$$

For all the bond types we have considered tangents have been taken in this manner. The theoretical justification for this method has already been discussed.

(ii) A possible method.

In an attempt to develop a possible method for the calculation of electron

distribution orbital charge equations have been derived for a wide range of bonds, including those involving atoms with π orbitals on them. The orbital charge equations are listed in the next chapter where we deal with parametrisation. Since the present method has been described at considerable length elsewhere[45], it is not the present intention to do any more than illustrate the main features of its use with reference to a relatively simple molecule like CH_3CH_2OH. (figure 3.2)

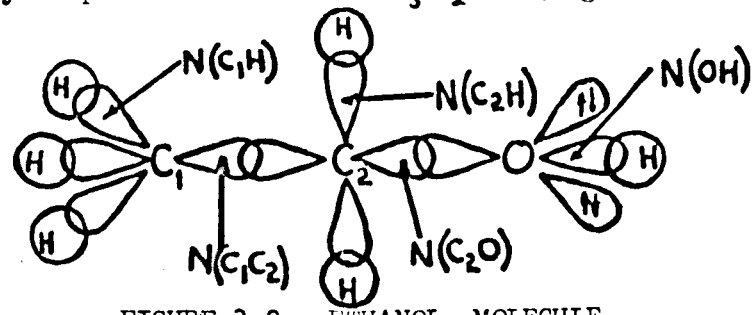


FIGURE 3.2. ETHANOL MOLECULE

An orbital charge equation is written for each bond in the molecule. The atoms in the molecule are usually numbered so that two atoms of any bond are in the order in which the atoms were placed when calculating the various orbital charge equations. Since the orbital charges of any bond are linked by the localisation condition

$$N(AB) + N(BA) = 2 \qquad (3.6)$$

this is quite in order. We now have a system of N orbital charge equations for the N orbital charges (or bonds). These equations can be solved by matrix algebra.

For ethanol, the orbital charge equations are as follows:-

$$\left.\begin{aligned}
N(C_1H) &= -k_{CH}\,(2N(C_1H) + N(C_1C_2)) + I_{CH} \\
N(C_1C_2) &= k_{CC}\,(2N(C_2H) + N(C_2O) - 3N(C_1H)) + 1{\cdot}0 \\
N(C_2H) &= -k_{CH}\,(N(C_2H) + N(C_2O) + 2 - N(C_1C_2)) + I_{CH} \\
N(C_2O) &= k_{OC}\,(N(OH) + 4) - k_{CO}\,(2N(C_2H) + 2 - N(C_1C_2)) + I_{CO} \\
N(OH) &= -k_{OH}\,(6 - N(C_2O)) + I_{OH}
\end{aligned}\right\} \qquad (3.7)$$

Collecting these equations into matrix form leads to equation (3.8)

$$
\begin{pmatrix}
1+2k_{CH} & k_{CH} & 0 & 0 & 0 \\
3k_{CC} & 1 & -k_{CC} & -k_{CC} & 0 \\
0 & -k_{CH} & 1+k_{CH} & k_{CH} & 0 \\
0 & -k_{CO} & k_{CO} & 1 & -k_{OC} \\
0 & 0 & 0 & -k_{OH} & 1
\end{pmatrix}
\begin{pmatrix}
N(C_1H) \\
N(C_1C_2) \\
N(C_2H) \\
N(C_2O) \\
N(OH)
\end{pmatrix}
=
$$

$$
\begin{pmatrix}
I_{CH} \\
1.0 \\
I_{CH} - 2k_{CH} \\
I_{CO} + 4k_{OC} - 2k_{CO} \\
I_{OH} - 6k_{OH}
\end{pmatrix}
\qquad (3.8)
$$

The time consuming part of this process is the setting up of matrices like the one shown above. Clearly if we have a large molecule containing various sorts of atoms, setting up such matrices by hand will be an error-prone as well as lengthy procedure. Consequently a program in Algol 60 has been written which will set up and solve the orbital charge equations for molecules containing a wide range of bond types. A listing of the program and details of its range of applicability is given in appendix III.

(iii) Functional Relations for Bond Orbital Charges.

It was remarked in section (i) of this chapter that orbital charge relations expressed the variation of orbital charge, say N(AB) in the bond A-B, with the charges in the other orbitals on A and B. To carry out an analysis one requires orbital charges N(AB) corresponding to different occupancies of the orbitals on atoms A and B.

In the present method these charges are calculated using the Hinze, Jaffe et al scheme. To do this we cast the equations of these workers into a more convenient form.

The orbital electronegativities of the orbitals ϕ_i and ϕ_j on atoms A and B respectively are given by

$$\frac{\partial E_i}{\partial n_i} = X_i = b_i + c_i n_i = \tfrac{1}{2}\left(3I_i^V - A_i^V \right) + n_i \left(A_i^V - I_i^V \right) \qquad (3\cdot9)$$

$$\frac{\partial E_j}{\partial n_j} = X_j = b_j + c_j n_j = \tfrac{1}{2}\left(3I_j^V - A_j^V \right) + n_j \left(A_j^V - I_j^V \right) \qquad (3\cdot10)$$

where $n_i = N(AB)$ $\quad n_j = N(BA)$

b_i , c_i , and b_j, c_j are coefficients appearing in the Hinze Jaffe equations. They depend on the charge occupancy of the orbitals on A and B, respectively, not involved in bond formation and on the effective nuclear charge of those atoms.

Using the principle of electronegativity equalisation

$$X_i = X_j \qquad (3\cdot11)$$

and the localisation condition one can write

$$b_i + c_i n_i = b_j + c_j \ (2 - n_i) \qquad (3\cdot12)$$

so that

$$n_i = \frac{b_j - b_i + 2c_j}{c_i + c_j} \qquad (3\cdot13)$$

Using relations (3·9) and (3·10) expression (3·13) becomes

$$n_i = N(AB) = \frac{3(I_{iA}^V - A_{jB}^V) + (I_{jB}^V - A_{iA}^V)}{2\,(I_{iA}^V + I_{jB}^V - A_{iA}^V - A_{jB}^V)} \qquad (3\cdot14)$$

Since I_{iA}^V , I_{jB}^V and A_{iA}^V , A_{jB}^V, the V.S.I.P.s and V.S.E.A.s of orbitals i and j, on atoms A and B respectively, depend on the total charge on those atoms, not including the charges in the orbitals involved in the bond A - B, we can easily obtain values of N(AB) corresponding to various values of N_T^A and N_T^B.

It is interesting to look at other functional relations for orbital charges. Firstly we deal with the simple Hückel theory. If we consider a localised two centre, two-electron bond A-B formed from orbitals ϕ_A on atom A and ϕ_B on atom B we can describe the doubly occupied MO as (3·15)

$$\bar{\phi} = C_A \phi_A + C_B \phi_B$$

The energy of the bond is given by

$$E = 2\,c_A^2\alpha_A + 2\,c_B^2\alpha_B + 4c_Ac_B\beta_{AB} \qquad (3.16)$$

where α_A and α_B are the Coulomb integrals of the orbitals ϕ_A and ϕ_B, and β_{AB} is the resonance integral between the two orbitals. Neglecting overlap, the orbital charges n_A and n_B in the valence orbitals ϕ_A and ϕ_B are

$$n_A = 2c_A^2 \qquad (3.17)$$

$$n_B = 2c_B^2 \qquad \text{(SEE APPENDIX II)} \qquad (3.18)$$

The energy of the bond is thus given by

$$E = n_A\alpha_A + n_B\alpha_B + 2\,(n_An_B)^{\frac{1}{2}}\,\beta_{AB} \qquad (3.19)$$

If we now partition E into the sum of two atomic energies

$$E = E_A + E_B \qquad (3.20)$$

where

$$E_A = n_A\alpha_A + (n_A(2-n_A))^{\frac{1}{2}}\,\beta_{AB} \qquad (3.21)$$

$$E_B = n_B\alpha_B + (n_B(2-n_B))^{\frac{1}{2}}\,\beta_{AB} \qquad (3.22)$$

we can use the definition of orbital electronegativity given by Hinze, Jaffe et al to write

$$\chi_A = \left(\frac{\partial E_A}{\partial n_A}\right) = \alpha_A + \beta_{AB}\,(1-n_A)\,((2-n_A)n_A)^{-\frac{1}{2}} \qquad (3.23)$$

$$\chi_B = \left(\frac{\partial E_B}{\partial n_B}\right) = \alpha_B + \beta_{AB}\,(1-n_B)\,((2-n_B)n_B)^{-\frac{1}{2}} \qquad (3.24)$$

Simple numerical analysis shows that

$$(1-n_A)\,((2-n_A)n_A)^{-\frac{1}{2}} = -m\,(n_A-1) \qquad (3.25)$$

so that equations (3.23) and (3.24) can be rewritten

$$\chi_A = \alpha_A + m\beta_{AB}\,(1-n_A) \qquad (3.26)$$

$$\chi_B = \alpha_B + m\beta_{AB}\,(1-n_B) \qquad (3.27)$$

Using the localisation condition equation and equating electronegativities

$$\alpha_A + m\beta_{AB}\,(1-n_A) = \alpha_B + m\beta_{AB}\,(n_A-1) \qquad (3.28)$$

and

$$\alpha_B - \alpha_A = 2m\beta_{AB}\,(1-n_A) \qquad (3.29)$$

from which

$$(1-n_A) = \frac{(\alpha_B-\alpha_A)}{2m\beta_{AB}} \qquad (3.30)$$

Digressing slightly - there are one or two interesting points about equation (3.30). Accepting the following significance of $\alpha_A\alpha_B$ and β_{AB},

within the context of the Hückel approximtion,

$$\alpha_A = \alpha + \delta_A \beta \qquad (3\cdot31)$$

$$\alpha_B = \alpha + \delta_B \beta \qquad (3\cdot32)$$

$$\beta_{AB} = \varepsilon_{AB} \beta \qquad (3\cdot33)$$

and noting that m is almost equal to unity

$$\frac{\alpha_B - \alpha_A}{2\beta_{AB}} = (1 - n_A) = \frac{(\delta_B - \delta_A)}{2\varepsilon_{AB}} \qquad (3\cdot34)$$

and $(1 - n_A)$ is identified with the ionicity of the bond, Q_{AB} (3·35)

$$Q_{AB} = \frac{\delta_B - \delta_A}{2\varepsilon_{AB}}$$

which is the expression that del Re and others [48] have used to determine charges on atoms in molecules and which was originally due to Mulliken [49]. Thus, we have, in a sense, given a theoretical backing to equation (3·35). We will have more to say about this equation in the next chapter.

Returning to equation (3·30), we can finally put

$$n_A = N(AB) = 1 + \frac{(\alpha_A - \alpha_B)}{2m\beta_{AB}} \qquad (3\cdot36)$$

In simple M.O. formalism, α_A and α_B are related to the V.S.I.P.s of orbitals ϕ_A and ϕ_B by [50]

$$\alpha_A = -I_A \qquad (3\cdot37)$$

$$\alpha_B = -I_B \qquad (3\cdot38)$$

so that

$$N(AB) = \frac{I_B - I_A + 2m\beta_{AB}}{2m\beta_{AB}} \qquad (3\cdot39)$$

We now go on to analyse an expression of orbital electronegativity cited by Baird, Sichel and Whitehead [51]

$$\chi_A = \left(\frac{\partial E_A}{\partial n_A}\right) = B_A^* + \tfrac{1}{2} n_A (\bar{A}_A + \bar{\Gamma}_{AB}) + \beta_{AB} (1 - n_A) ((2 - n_A) n_A)^{-\frac{1}{2}} \qquad (3\cdot40)$$

$$\chi_B = \left(\frac{\partial E_B}{\partial n_B}\right) = B_B^* + \tfrac{1}{2} n_B (\bar{A}_B + \bar{\Gamma}_{AB}) + \beta_{AB} (1 - n_B) ((2 - n_B) n_B)^{-\frac{1}{2}} \qquad (3\cdot41)$$

which we derived from Klopman's L.CAO.M.O. SCF method [52] B_A^* is the

interaction energy of an electron in orbital ϕ_A with its own nucleus, inner-shell and other valence shell electrons on A, A_A^- is the repulsion energy of two electrons of opposed spin in orbital ϕ_A, and $-\Gamma_{AB}$ is the repulsion energy between an electron in ϕ_A and one in ϕ_B.

Equalising electronegativities in the manner shown above gives

$$n_A = \frac{2\,(B_A^* - B_B^* - A_B^- - \Gamma_{AB} + 2m\beta_{AB})}{(4m\beta_{AB} - A_A^- - A_B^- - 2\Gamma_{AB})} \qquad (3.42)$$

Using the Pariser Parr approximation for A_A^- and A_B^-

$$A^- = I - A \qquad (3.43)$$

and equating B_A^* and B_B^* to the respective V.S.I.P.s with opposite sign

$$B^* = -I \qquad (3.44)$$

and $-\Gamma_{AB}$ to γ_{AB}, the two centre Coulomb repulsion integral gives

$$n_A = N(AB) = 2\,\frac{(I_A - A_B - \gamma_{AB} - 2m\beta_{AB})}{(I_A - A_A + I_B - A_B - 2\gamma_{AB} - 4m\beta_{AB})} \qquad (3.45)$$

Baird et al quote another expression which may be obtained from Klopman's expressions by further approximation[52,44], which takes the form

$$X_A = \left(\frac{\partial E_A}{\partial n_A}\right) = B_A^* + \tfrac{1}{2} n_A A_A^- \qquad (3.46)$$

which becomes, using relations (3.43) and (3.44)

$$X_A = -I_A + \tfrac{1}{2} n_A (I_A - A_A) \qquad (3.47)$$

It was recognised by Moffitt some time ago[53] and it has been frequently noted by others[54,55] that this is just the atomic part of the diagonal element of the S.C.F. Hamiltonian, Ferreira has commented that this expression does not conform to the correct quantum mechanical expression for the energy of a system containing n electrons because integration of (3.47) with respect to n_A leads to

$$E_A = -I_A n_A - \tfrac{1}{4} n_A^2 \quad (I_A - A_A) \qquad (3.48)$$

whereas the correct quantum mechanical expression should read[56]

$$E_A = -I_A n_A - \tfrac{1}{2} n_A (n_A - 1) \quad (I_A - A_A) \qquad (3.49)$$

However, using equation (3.48) for X_A and a similar one for X_B leads, on equalising electronegativities to the functional form[56,57]

$$n_A = 2(I_A - A_B) / (I_A - A_A + I_B - A_B) \qquad (3.50)$$

In their study of the M.O. method as applied to diatomic molecules, Jenkins and Pedley obtained the relation[57]

$$\Delta = n_A - 1 = \frac{(I_A - A_A - I_B - A_B)}{(I_A - A_A + I_B - A_B - 2\frac{e^2}{r} - \frac{2S_{AB}}{(1+S_{AB})}(I))} \quad (3.51)$$

where $(I) = \frac{1}{2}n_A\gamma_{AA} + \frac{1}{2}n_B\gamma_{BB} + (a:AA) - \sum G_{AD} + (b:BB) - \sum G_{Bc} - \gamma_{AB}$ (3.52)

($\sum G_{AB}, \sum G_{Bc}$ are Coulomb - exchange terms involving other orbitals on A and B; $(a:AA)$ is nuclear attraction of atom A for electron in ϕ_A)

Rearrangement gives the following form for n_A

$$n_A = \frac{2(I_A - A_B - \frac{e^2}{r} - S_{AB}/(1+S_{AB})(I))}{(I_A - A_A + I_B - A_B - 2\frac{e^2}{r} - 2S_{AB}/(1+S_{AB})(I))} \quad (3.53)$$

where $\frac{e^2}{r}$ is the point charge approximation for the two centre Coulomb integral γ_{AB}. We notice that this expression is similar in form to equation (3.42). Indeed (I) represents integrals closely related to β_{AB} . Complete neglect of overlap integral S_{AB} and of β_{AB} cause the two expressions to become identical . Furthermore, Jenkins and Pedley noticed that for the diatomic molecules studied[57]

$$\frac{e^2}{r} \simeq -\frac{S_{AB}}{(1+S_{AB})}(I) \quad (3.54)$$

so that equation (3.53) reduces to equation (3.42).

Ferreira has made a similar observation[56].

Much work on 2 electron bonds in molecules has been done also by Tong[58] on gallium acceptor-donor complexes, and by Ferreira[56] on the diatomic hydrogen halides. Ferreira derives the following equation for the orbital charge n_i, in the bond AB formed from the A.O.s i on A and j on B:

$$n_i = \frac{2(I_i - A_j - 2\beta_{ij}(1-x^2)^{-\frac{1}{2}} - \frac{e^2}{r_{ij}})}{(I_i + I_j - A_i - A_j) - 4\beta_{ij}(1-x^2)^{-\frac{1}{2}} - 2\frac{e^2}{r_{ij}}} \quad (3.55)$$

where x^2 is the ionic bond order.

Once again we notice the same basic form of expression. If

$$-2\beta_{ij}(1-x^2)^{-\frac{1}{2}} - \frac{e^2}{r_{ij}} = 0 \quad (3.56)$$

then the equation reduces to equation (3.42).

Ferreira was concerned with finding a suitable two - electron Hamiltonian for the process.

$$A_V B_V^{2+} (\uparrow_e) + 2e \xrightarrow{\varepsilon_{M.O.}} AB (\uparrow_e) \qquad (3.57)$$

in order to make an equivalence between H.M.O. methods and methods involving the differentiation of bond or electronic energies. He, (and Tong, too) pointed out that the energies of the two electrons are different and that to investigate two electron properties such as bond energies, dipole moments, etc., an average two-electron Hamiltonian should be used.

So far we have dealt mainly with diatomic molecular theory. We now examine the effect of subjecting the energy expression of a fairly full SCF.MO treatment to a partitioning among atoms. Choosing the CNDO method of Pople et al[93], the total energy of a molecule is given, in this theory by

$$E_{total} = \sum_A E_A + \sum_{A<B} E_{AB} \qquad (3.58)$$

where E_A, and E_{AB} are monatomic and diatomic energies respectively. For just two A.O.s i and j on atoms A and B respectively involved in bond formation, the monatomic energies are given by

$$E_A = -n_i I_i + \tfrac{1}{4} n_i^2 (I_i - A_i) \qquad (3.59)$$

$$E_B = -n_j I_j + \tfrac{1}{4} n_j^2 (I_j - A_j) \qquad (3.60)$$

and the diatomic energy by

$$E_{AB} = 4(n_i n_j)^{\frac{1}{2}} \beta_{ij} - n_i n_j \gamma_{ij} \qquad (3.61)$$

We now partition equation (3.61) between the two atoms and carry out electronegativity equalisation.

$$E' = 2 (n_i n_j)^{\frac{1}{2}} \beta_{ij} - \tfrac{1}{2} n_i n_j \gamma_{ij} \qquad = \tfrac{1}{2} E_{AB} \qquad (3.62)$$

We now add this quantity to E_A and to E_B and use the expression $n_i + n_j = 2$ to express the "new" atomic energies E_A' and E_B' in terms of n_i only and n_j only, respectively.

Thus

$$E'_A = -n_i I_i + \tfrac{1}{4} n_i^2 \ (I_i - A_i) + (2\ (2n_i - n_i)^{\frac{1}{2}} \beta_{ij} - \tfrac{1}{2}\ (2n_i - n_i^2)\gamma_{ij} \qquad (3.63)$$

$$E'_B = -n_j I_j + \tfrac{1}{4} n_j^2 (I_j - A_j) + 2\ (2n_j - n_j^2)^{\frac{1}{2}} \beta_{ij} - \tfrac{1}{2}\ (2n_j - n_j^2)\gamma_{ij} \qquad (3.64)$$

Differentiating the above expression with respect to n_i and n_j respectively gives, eventually:-

$$n_i = \frac{2\ (I_i - A_j - 4\beta_{ij} + 2\gamma_{ij})}{(I_i + I_j - A_i - A_j - 8\beta_{ij} + 4\gamma_{ij})} \qquad (3.65)$$

This equation, too, falls in with the same general formalism we have found throughout this analysis. It reduces to equation (3·50) if

$$-4\beta_{ij} + 2\gamma_{ij} = 0 \qquad (3.66)$$

It is interesting to note that expressions (3·42), (3·53), (3·55) and (3·65) all generate within the limits of the approximations employed on equation for n_A of the form (3·50). In deriving equation (3·53) - and consequently (3·50) - Jenkins and Pedley considered the valence electrons in ϕ_A and ϕ_B as having "randomised" spin. This statement is equivalent to the statement that the two bonding electrons each spend half their time in orbital ϕ_A and half their time in orbital ϕ_B. This, Baird, Sichel and Whitehead have pointed out[51], amounts to complete neglect of electron correlation. On the other hand the Hinze - Jaffe - Whitehead expression results from a complete correlation of electron motion. Baird, Sichel and Whitehead attempted to find a "middle road" approach between the two extremes and have suggested an equation representing partial correlation of electronic motion which takes the following form

$$E_A = \tfrac{1}{4}\ (5\ I_A - A_A) n_A + \tfrac{3}{8}\ (A_A - I_A)\ n^2_A \qquad (3.56)$$

giving

$$\chi_A = \frac{(\partial E_A)}{(\partial n_A)} = \tfrac{1}{4}(I_A - A_A) + \tfrac{3}{4}(A_A - I_A) \qquad (3.57^a)$$

from which one obtains

$$n_A = N(AB) = \frac{5(I_A - A_B) + (I_B - A_A)}{3(I_A + I_B - A_A - A_B)} \qquad (3.58^a)$$

The non-correlated, partially correlated and totally correlated functions for n_A can be generalised by

$$n_A = N(AB) = \frac{C_1(I_A - A_B) + C_2(I_B - A_A)}{(I_A + I_B - A_A - A_B)} \qquad (3.59)$$

where C_1 and C_2 are constants. The values of these constants for the three types of functions are given in table 3.1

C	C	Type of Function
2	0	Non - Correlated
5/3	1/3	Partially - Correlated
3/2	1/2	Totally - Correlated

Table 3·1 Coefficients in equation 3.59^a

In the next chapter we shall look at the effect of using the three types of expression, on parametrisation.

An interesting point about Parks' and Parr's approach concerns the polarity Q_k of the K^{th} bond[39]. The following expression relating Q_k to the Coulomb integrals and the Coulomb repulsion integrals of the orbitals a and b forming the K^{th} bond can be derived (see Appendix I)

$$Q_K = \frac{(\alpha_{Kb} - \alpha_{Ka}) + \tfrac{1}{2}(\gamma_{KbKb} - \gamma_{KaKa})}{\sqrt{1 - S^2}\left\{-2\beta + \frac{1}{4\sqrt{1 - S^2}}(\gamma_{KaKa} + \gamma_{KbKb} - 2\gamma_{KaKb})\right\}} \qquad (3.60^a)$$

where the α_K's are the Coulomb integrals, the γ_K's the Coulomb repulsion integrals, S the overlap integral between orbitals a and b, and β a resonance integral.

If we now make the assumption that

$$-2\beta - \frac{1}{2\sqrt{1-S^2}}\gamma_{KaKb} = 0 \qquad (3.61^a)$$

equation (3.60^a) becomes

$$Q_K = \frac{4\,(\alpha_{Kb} - \alpha_{Ka}) + 2\,(\gamma_{KbKb} - \gamma_{KaKa})}{(\gamma_{KaKa} + \gamma_{KbKb})} \qquad (3.62^a)$$

The second assumption we make is that Q_K, the polarity is the ionicity, in which case

$$Q_K = n_K^a - 1 \qquad (3.63^a)$$

where n_k^a is the electronic charge density in orbital a in the K^{th} bond. In the following argument the subscripts K will be dropped. Equation (3.62^a) can now be rewritten as

$$n_a = \frac{4\,(\alpha_b - \alpha_a) + 3\gamma_{bb} - \gamma_{aa}}{(\gamma_{aa} + \gamma_{bb})} \qquad (3.64^a)$$

The final step involves a third assumption

$$\left.\begin{aligned} \alpha_a &= -I_a \\ \alpha_b &= -I_b \\ \gamma_{aa} &= I_a - A_a \\ \gamma_{bb} &= I_b - A_b \end{aligned}\right\} \qquad (3.65^a)$$

where the I's and A's are V.S.I.P.s and V.S.E.A.s substitution of (3.65^a) into (3.64^a) gives

$$n_a = \frac{3\,(I_a - A_b) - (I_b - A_b)}{(I_a + I_b - A_a - A_b)} \qquad (3.66^a)$$

Equation (3.66^a) expresses n_a, the electronic charge in orbital a in bond K, as a function of the V.S.I.P.s and V.S.E.A.s of the orbitals a and b comprising bond K.

Before leaving this chapter we will look at two other expressions which can also be derived from (3.60^a)

The assumption 1′ is now made, that

$$-2\beta - \frac{1}{4\sqrt{1-S^2}}\left\{\gamma_{bb} + \gamma_{aa} + 2\gamma_{ab}\right\} = 0 \qquad (3.67^a)$$

Applying the second assumption, 2′, (i.e. equation (3.63^a)) we obtain

$$n_a = \frac{2(\alpha_b - \alpha_a) + 2\gamma_{bb}}{(\gamma_{aa} + \gamma_{bb})} \qquad (3.68^a)$$

Upon adoption of the third assumption, 3′, (i.e. equation (3.65^a)) the following expression is arrived at

$$n_a = \frac{2(I_a - A_b)}{(I_a + I_b - A_a - A_b)} \qquad (3.69^a)$$

which is the non-correlated expression obtained earlier and mentioned in the work of several authors.

The interesting point is that the final form of the expression depends upon the treatment of the denominator of equation (3.60^a). It is difficult to decide which assumption is the most valid because of the nature of β, and indeed differing molecular situations may validate differing approximations so in this sense both choices may be conditionally acceptable. However the fact that the expressions turn out to be similar to those we have already met leads us to feel that our treatment can be placed in the context of more rigorous treatments.

A final word on the equations derivable from Parks' and Parr's theory: if we make the assumption 1″ that

$$-2\beta - \frac{1}{4\sqrt{1-S^2}}(3\gamma_{bb} + 3\gamma_{aa} + 2\gamma_{ab}) = 0 \qquad (3.70^a)$$

together with assumptions 2′ and 3′ we obtain

$$n_a = \frac{3(I_a - A_b) + (I_b - A_b)}{2(I_a + A_b - A_a - A_b)} \qquad (3.71^a)$$

which is the same as the correlated functional form derived earlier from simple valence state considerations.

It seems to be the case that equations (3.66), (3.69) and (3.71) represent three limiting types. The types obviously depend on the nature of the bond in the molecule we are considering.

CHAPTER 4

PARAMETERS

(i) Parametrisation Scheme.

Consider a bond formed between atoms X and Y in which orbital i on X and orbital j on Y are involved. The orbital charge equation

$$N(XY) = k_{YX} N_T^Y - k_{XY} N_T^X + I_{XY} \qquad (4.1)$$

states that N(XY), the orbital charge in the bond X-Y, is a function of the occupancies of the other orbitals on atoms X and Y not involved directly in the bond X-Y. Del Re's method, basically an inductive approach, involves a concept not unlike that of orbital charges[45]. In the latter's work and those of others using Del Re's method[46-48], the inductive parameters appearing in equations analogous to (4.1) are obtained by optimising the calculated dipole moments in a series of small molecules.

The method of parametrisation used in the present method is based on the identification of k_{xy} and k_{yx} with the rate of change of electronic charge on atoms X and Y respectively, excluding the charges in orbitals i and j respectively.[60].

That is

$$k_{XY} = \left(\frac{\partial N(XY)}{\partial N_T^X}\right)_{N_T^Y \text{ CONSTANT}} \qquad (4.2)$$

$$k_{YX} = \left(\frac{\partial N(YX)}{\partial N_T^Y}\right)_{N_T^X \text{ CONSTANT}} \qquad (4.3)$$

There are two possible ways of finding the k_{XY}'s and k_{YX}'s. Firstly we can examine charge distribution calculated by a theoretical method presently in use. Secondly we can use the functional relations, discussed in chapter 3

to obtain values of N(XY) as a function of N_T^X and N_T^Y for the isolated bond X-Y.

The second approach has already been discussed in the author's M.Sc. thesis. Summarising, the analysis runs as follows. N(XY) is a function of I_x, I_y, A_x and A_y, the valence state ionisation energies, which are functions of the total charges on atoms X and Y minus the charges in the bond. N(XY) is plotted against N_T^X and against N_T^Y. It is usual to consider the hypothetical diatomics shown in figure (4·1).

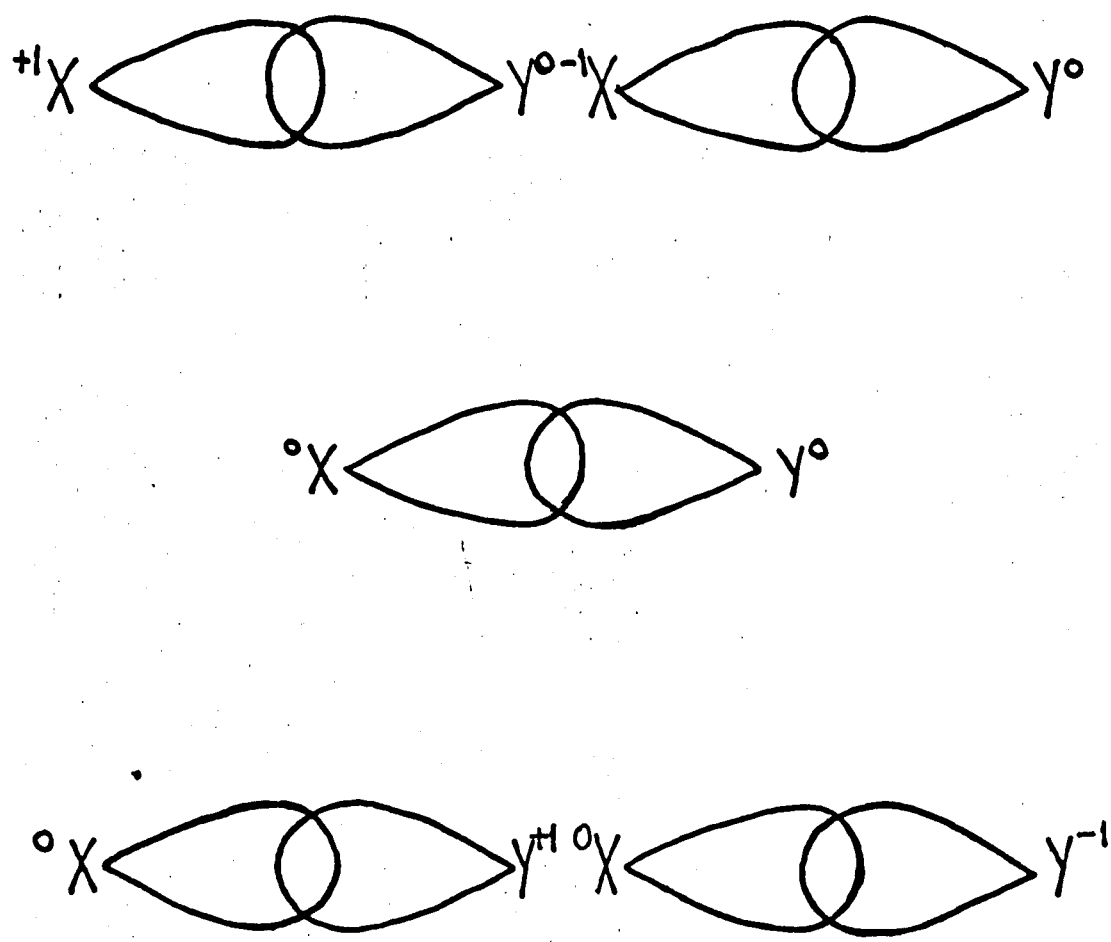


FIGURE 4.1. HYPOTHETICAL "DIATOMICS" CONSIDERED IN THE ANALYSIS OF N(XY)

Two sets of quadratic equations are obtained.

$$\begin{aligned}
&A + B\,N_T^X\,(q_x = +1) + C\,N_T^{X2}\,(q_x = +1) = N(XY)\,(q_x = +1)\\
&A + B\,N_T^X\,(q_x = 0) + C\,N_T^{X2}\,(q_x = 0) = N(XY)\,(q_x = 0)\\
&A + B\,N_T^X\,(q_x = -1) + C\,N_T^{X2}\,(q_x = -1) = N(XY)\,(q_x = -1)\\
&\quad (N_T^Y \text{ constant at } q_y = 0)
\end{aligned} \tag{4.4}$$

$$\begin{aligned}
&A' + B'\,N_T^Y\,(q_y = +1) + C'\,N_T^{Y2}\,(q_y = +1) = N(XY)\,(q_y = +1)\\
&A' + B'\,N_T^Y\,(q_y = 0) + C'\,N_T^{Y2}\,(q_y = 0) = N(XY)\,(q_y = 0)\\
&A' + B'\,N_T^Y\,(q_y = -1) + C'\,N_T^{Y2}\,(q_y = -1) = N(XY)\,(q_y = -1)\\
&\quad (N_T^X \text{ constant at } q_x = 0)
\end{aligned} \tag{4.5}$$

q_x and q_y are net total charges and A,B,C, A',B',C', are determined in a straightforward manner. The resulting quadratics

$$N(XY) = A + B\,N_T^X + C\,N_T^{X2} \tag{4.6}$$

$$N(XY) = A' + B'\,N_T^Y + C'\,N_T^{Y2} \tag{4.7}$$

are then differentiated with respect to N_T^X and N_T^Y respectively to give

$$\left(\frac{\partial N(XY)}{\partial N_T^X}\right)_{N_T^Y \text{ CONST.}} = B + 2C\,N_T^X \tag{4.8}$$

$$\left(\frac{\partial N(XY)}{\partial N_T^Y}\right)_{N_T^X \text{ CONST.}} = B' + 2C'\,N_T^Y \tag{4.9}$$

Upon insertion of N_T^X $(q_x = 0)$ and N_T^Y $(q_y = 0)$ into (4.8) and (4.9) respectively, k_{xy} and K_{yx} are obtained directly.

(ii) Evaluation of Parameters.

Firstly we consider the charges appearing in the literature for various molecules. Extended Hückel calculation results[61] are used to examine N(C(te) - H(Is)) as a function of N_T^C, the total charge on the carbon minus that due to the C-H bond. The values chosen are shown in table 4.1 and a plot of the E.H.T. orbital charge N(CH) against N_T^C is presented in figure 4.2

(N.B. In plots involving orbital charges or total charges or both the units are numbers of electrons)

MOLECULE		N (CH)	N_T^C
CH_4	1.	1·126	3·377
$H_3\overset{a}{C}-\overset{b}{C}H_2-CH_3$	2a.	1·110	3·233
	2b.	1·095	3.069
$(H_3\overset{a}{C})\overset{b}{C}H$	3a.	1·111	3·247
	3b.	1·082	2·926
$H_3\overset{a}{C}-\overset{b}{C}H_2-CH_2-CH_3$	4a.	1·110	3·232
	4b.	1·096	3.085
$(H_3C)_4C$	5.	1·113	3·260
$(H_3\overset{a}{C})_2-\overset{b}{C}H-CH-(CH_3)_2$	5a.	1·117	3·257
	5b.	1·085	2·955
$H_3\overset{a}{C}-\overset{b}{C}H_2-\overset{c}{C}H-(\overset{d}{C}H_3)_2$	6a.	1·122	3·256
	6b.	1·098	3·097
	6c.	1·083	2·940
	6d.	1·117	3·254

TABLE 4.1 ORBITAL CHARGES, N(CH), AND TOTAL CHARGES ON ATOMS, N_T^C, OBTAINED FROM E.H.T. CALCULATIONS.

Taking the tangent to the curve in figure 4.2 at the point $N_T^C = 3.0$ gives

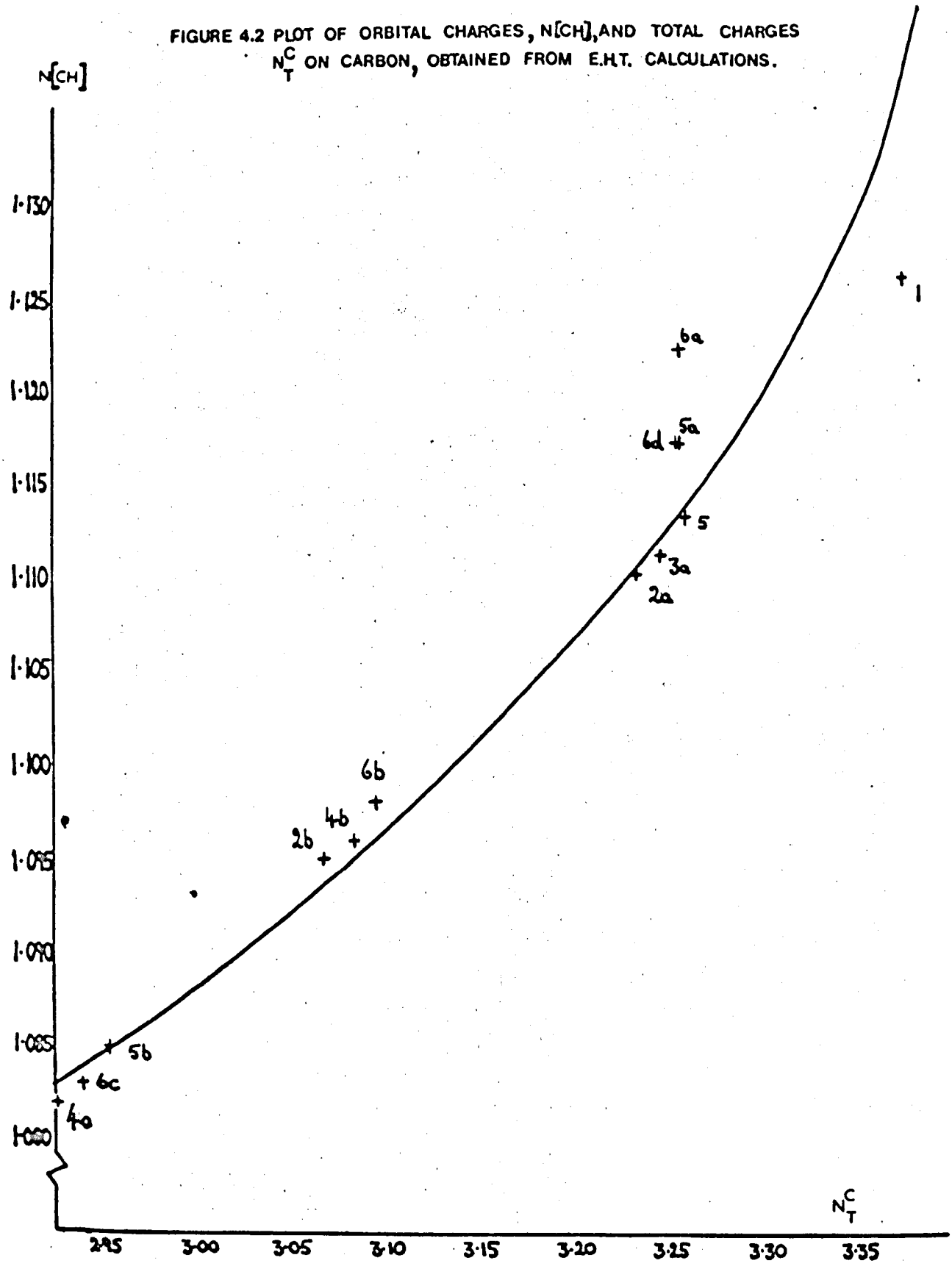
$$\left(\frac{\partial N(CH)}{\partial N_T^C}\right)_{N_T^C=3.0} = k_{CH} = 0.0759 \qquad (4.10)$$

and the resulting orbital charge expression is

$$N(CH) = 0.0759\ N_T^C + 0.859 \qquad (4.11)$$

Secondly we examine parameters obtained from three of the functional relationships discussed in chapter 3 viz. equations (3·14), (3·58) and (3·50). These three equations are the correlated, partially correlated and non-correlated functions.

FIGURE 4.2 PLOT OF ORBITAL CHARGES, N[CH], AND TOTAL CHARGES N_T^C ON CARBON, OBTAINED FROM E.H.T. CALCULATIONS.



For the carbon (te te te te) - nitrogen (te te te te^2) sigma bond, for example, the three equations are

$$N(CN) = 0.3448\, N_T^N - 0.3658\, N_T^C + 0.5912 \qquad (4.12)$$

$$N(CN) = 0.4598\, N_T^N - 0.4878\, N_T^C + 0.4549 \qquad (4.13)$$

$$N(CN) = 0.6897\, N_T^N - 0.7317\, N_T^C + 0.1824 \qquad (4.14)$$

The functions (3.14), (3.58)[a] and (3.50) for the C-N bond are shown graphically in figures 4.3 and 4.4. The partially correlated and non-correlated functions show a much more drastic change in N(CN) with charge than is the case with the completely correlated function.

In table 4.2 is presented a list of the parameters evaluated from the three functions for a wide range of bond types. One notes that

$$k_{xy(3)} = 2k_{xy(1)} \qquad (4.15)$$

$$k_{yx(3)} = 2k_{yx(1)} \qquad (4.16)$$

$$I_{xy(3)} = 2I_{xy(1)}^{-1} \qquad (4.17)$$

The non-correlated, k_{xy} and k_{yx}, parameters are always larger than the partially correlated ones, which in turn are larger than the correlated values. Where the first atom of the bond is less electronegative than the second.

$$I_{xy(1)} > I_{xy(2)} > I_{xy(3)} \qquad (4.18)$$

and the reverse is true when the first atom is more electronegative than the second.

(iii) Trial Calculations.

All three types of parameter have been used to compute charges in a number of small molecules. The results are presented in figure 4.5 for comparison.

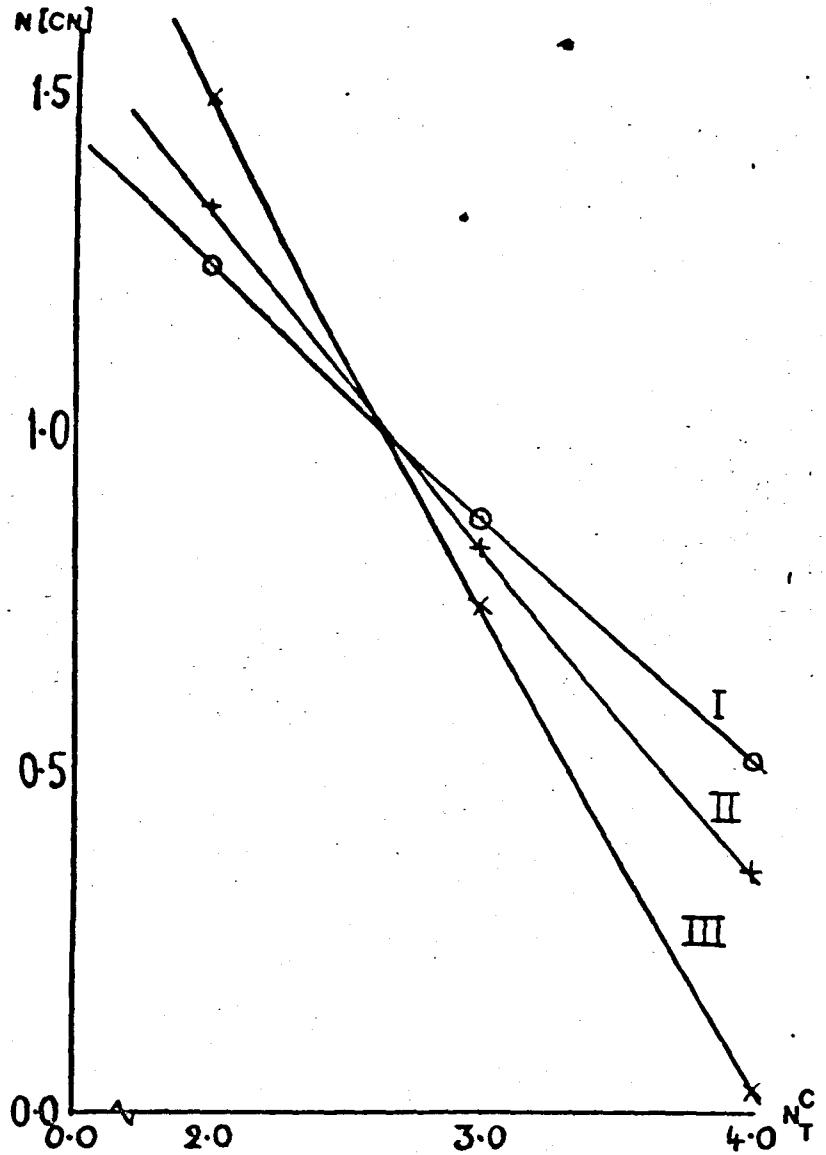


FIGURE 4.3 PLOT OF N[CN] AGAINST N_T^C, THE TOTAL CHARGE ON CARBON.

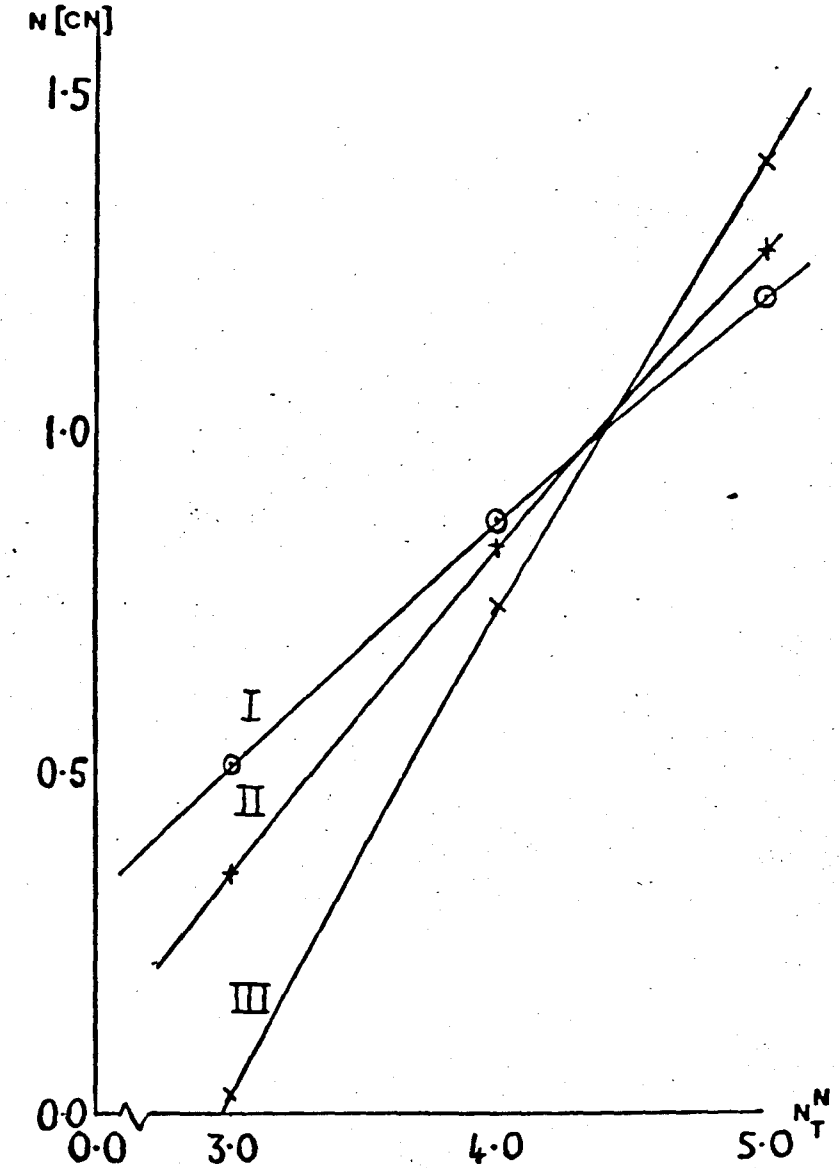


FIGURE 4.4 PLOT OF N[CN] AGAINST N_T^N, THE TOTAL CHARGE ON NITROGEN.

TABLE 4.2 PARAMETERS FOR VARIOUS SIGMA BONDS CALCULATED USING RELATIONS 3.14 (1), 3.58 (2), AND 3.50 (3).

BOND TYPE X - Y		K_{xy}	K_{yx}	I_{xy}
C(te)–H(1s)	1.	0.3729		2.1493
	2.	0.4972		2.5324
	3.	0.7457		3.2986
C(te)–C(te)		0.3709	0.3709	1.0000
		0.4945	0.4945	1.0000
		0.7417	0.7417	1.0000
C(te)–N(te)		0.3658	0.3148	0.5912
		0.4878	0.4598	0.4549
		0.7317	0.6897	0.1824
C(te)–N(2p)		0.3693	0.4237	0.4366
		0.4925	0.5650	0.2488
		0.7387	0.8474	-0.1269
C(te)–O(te)		0.3275	0.3896	-0.2026
		0.4367	0.5195	-0.6035
		0.6550	0.7793	-1.4052
C(te)–O(2p)		0.3506	0.4459	-0.2361
		0.4674	0.5945	-0.6482
		0.7011	0.8918	-1.4722
C(te)–S(te)		0.4256	0.3745	0.3146
		0.5674	0.4993	0.0862
		0.8511	0.7489	-0.3707
C(te)–S(2p)		0.4221	0.3782	0.4009
		0.5628	0.5042	0.2011
		0.8442	0.7563	-0.1983
N(te)–H(1s)		0.3454		2.5395
		0.4605		3.0526
		0.6908		4.0789
N(2p)–H(1s)		0.4245		2.7051
		0.5660		3.2735
		0.8490		4.4103
O(te)–H(1s)		0.3914		3.2222
		0.5219		3.9629
		0.7828		5.4444
O(2p)–H(1s)		0.4185		3.3304
		0.5980		4.1072
		0.8971		5.6609
S(te)–H(1s)		0.3785		3.0179
		0.5047		3.6906
		0.7571		5.0359
S(2p)–H(1s)		0.3835		2.9266
		0.5113		3.5688
		0.7669		4.8532
C(tr)–H(1s)		0.3602		2.1413
		0.4802		2.5217
		0.7203		3.2826

BOND TYPE X - Y		K_{xy}	K_{yx}	I_{xy}
C(tr)–C(tr)	1.	0.3561	0.3561	1.0000
	2.	0.4748	0.4748	1.0000
	3.	0.7122	0.7122	1.0000
C(tr)–C(te)		0.3581	0.3689	0.9978
		0.4775	0.4919	0.9970
		0.7162	0.7378	0.9955
C(tr)–$\dot{N}$(tr)		0.3488	0.3258	0.6034
		0.4651	0.4344	0.4713
		0.6977	0.6515	0.2069
C(tr)–$\ddot{N}$(tr)		0.3553	0.2874	0.7933
		0.4738	0.3832	0.7244
		0.7206	0.5748	0.5866
$\dot{N}$(tr)–$\dot{N}$(tr)		0.3267	0.3267	1.0000
		0.4356	0.4356	1.0000
		0.6533	0.6533	1.0000
$\dot{N}$(tr)–$\ddot{N}$(tr)		0.3311	0.2928	1.1722
		0.4414	0.3904	1.2296
		0.6622	0.5855	1.3444
$\ddot{N}$(tr)–H(1s)		0.2853		2.3260
		0.3803		2.7681
		0.5705		3.6521
C(tr)–O(tr) S_o=0.333		0.3187	0.4025	-0.3082
		0.4249	0.5367	-0.7443
		0.6374	0.8050	-1.6165
C(tr)–O(tr) S_o=0.0		0.3386	0.4523	-0.2750
		0.4515	0.6031	-0.7000
		0.6773	0.9046	-1.5500
C(tr)–F(2p)		0.3233	0.4735	-0.9805
		0.4311	0.6313	-1.6407
		0.6466	0.9470	-2.9610
C(tr)–Cl(3p)		0.3914	0.3817	-0.1318
		0.5258	0.5089	-0.5090
		0.7887	0.7634	-1.2635
O(tr)–H(1s) S_o=0.333		0.4058		3.3377
		0.5411		4.1169
		0.8116		5.6754
O(tr)–H(1s) S_o=0.0		0.4582		3.3787
		0.6110		4.1716
		0.9165		5.7574
$\ddot{N}$(tr)–$\dot{O}$(tr) S_o=0.333		0.2777	0.4022	-0.0404
		0.3702	0.5362	-0.3872
		0.5553	0.8043	-1.0808
$\ddot{N}$(tr)–$\dot{O}$(tr) S_o=0.0		0.2774	0.4490	-0.0473
		0.3699	0.5987	-0.3965
		0.5548	0.8981	-1.0947

The three methods all give qualitatively and quantitatively similar results for the alkanes, methane and ethane. In propane, the non-correlated result shows reversal of net charge on the carbon atoms. In butane, the partially - correlated result shows charge reversal on the carbon atoms.

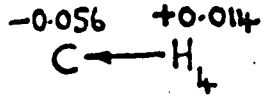
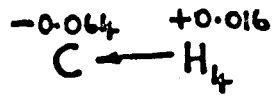
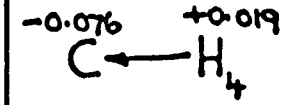
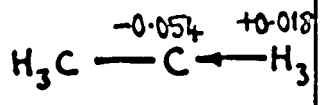
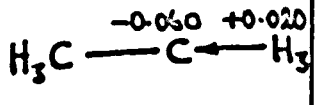
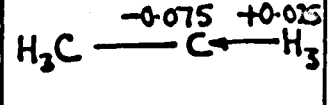
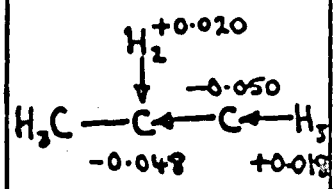
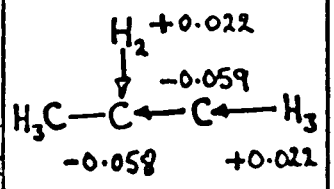
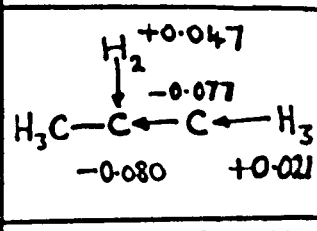
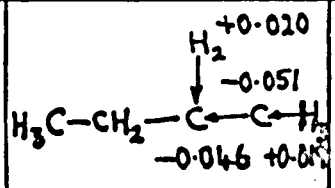
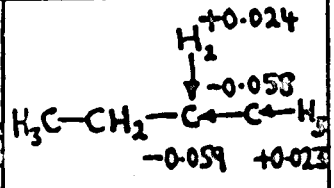
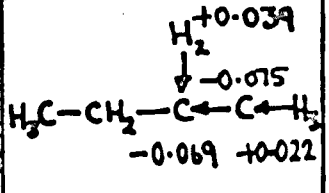
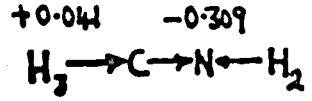
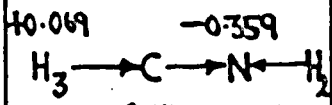
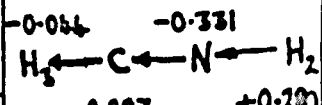
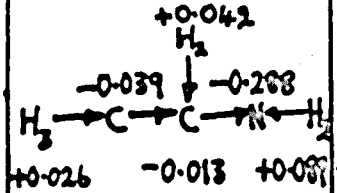
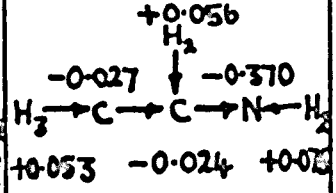
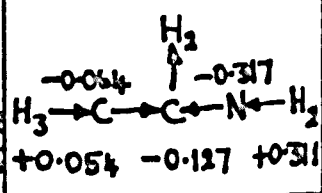
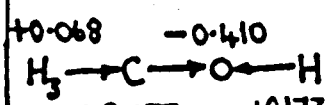
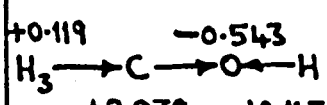
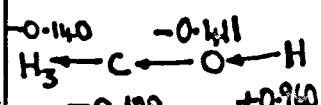
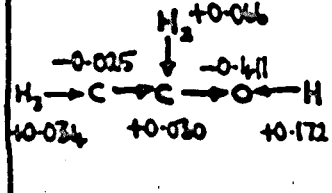
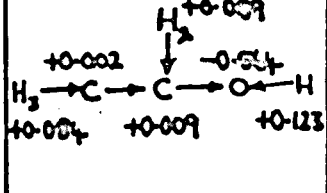
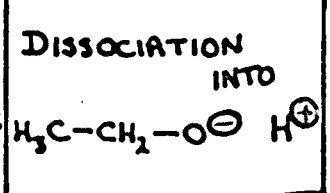
MOLECULE	CORRELATED	PARTIALLY-CORRELATED	NON-CORRELATED
METHANE			
ETHANE			
PROPANE			
BUTANE			
METHYLAMINE			
ETHYLAMINE			
METHANOL			
ETHANOL			

FIGURE 4.5 COMPARISON OF COMPUTED NET CHARGES AND CHARGE TRANSFERS OBTAINED USING EQUATIONS 3.14, 3.58[a] AND 3.50.

However, it is in the heteroatom - containing molecules that we get a clearer picture of what is happening. In all four of the latter molecules the heteroatom is a strong attracter of charge from the neighbouring carbon and hydrogen atoms, the oxygen atom showing this effect to a greater degree than nitrogen. In fact, the heteroatom draws charge from all parts of the molecule. In the correlated and partially-correlated results the charge transfer to the heteroatom from its hydrogen atoms is approximately the same as the charge transfer from its neighbouring carbon atom. However, in the non-correlated results we observe that the charge drift to the heteroatom from the former source is so great that it reverses the direction of charge transfer in the neighbouring C-N and C-H bonds.

Consequently in the last named calculations the hydrogen atoms on the neighbouring carbon bear negative charges, while the carbon atom itself assumes high negative charges. The terminal hydrogen atoms have large, but positive net charges. For ethanol, the non-correlated calculation predicts that the molecule exists as proton and ethanoate ion. For obvious reasons, therefore, we do not use the non-correlated parameters.

Considering the partially-correlated results, the charges - and charge transfers - computed are larger than those obtained from the correlated function although qualitatively the two sets of results are similar. It is felt, nonetheless, that overall the correlated function leads to better results. The charge drifts in the partially-correlated results are too large, and taking earlier results on chloroparaffins[64] into account, the correlated method provides a more consistent scheme.

CHAPTER 5

Some Calculations of Sigma bonded Molecules.

An attempt is made in this chapter to relate certain calculations of charges which have been made, with experimental quantities and to compare such charges with those resulting from other methods of calculation.

(i) The small molecules H_2O and NH_3

One of the main features of the proposed method is that the parameters used refer to atoms in particular valence states. In fact, the charges calculated can depend very much on the valence states of the atoms in the molecule, because V.S.I.P.s and V.S.E.A.s are sensitive to hybridisation. Figure 5.1 shows how the V.S.I.P. and V.S.E.A. of an isolated oxygen atom vary with the s orbital character, S, of the half-filled orbital on the oxygen atom. The variation of the orbital charge, N(OH), in an isolated O-H bond, with S is illustrated in figure 5.2.

The orbital charge equations for the water molecule (figure 5.3) are very simple. There is, in fact, only one of them.

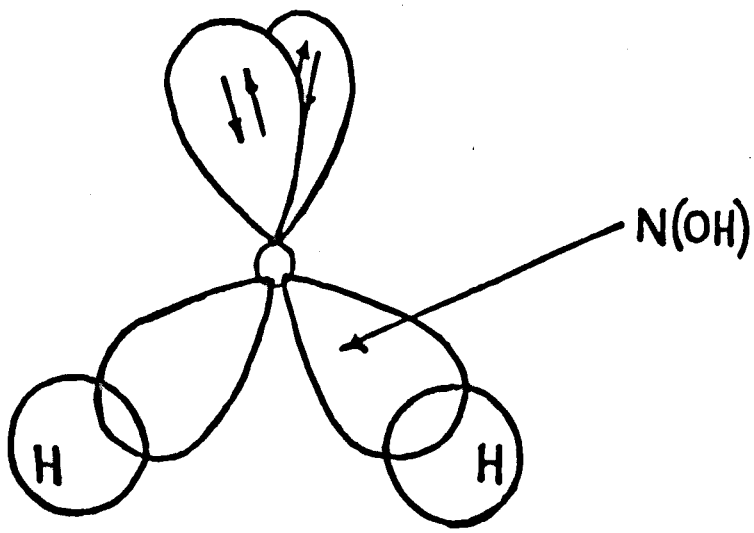


FIGURE 5.3. WATER MOLECULE

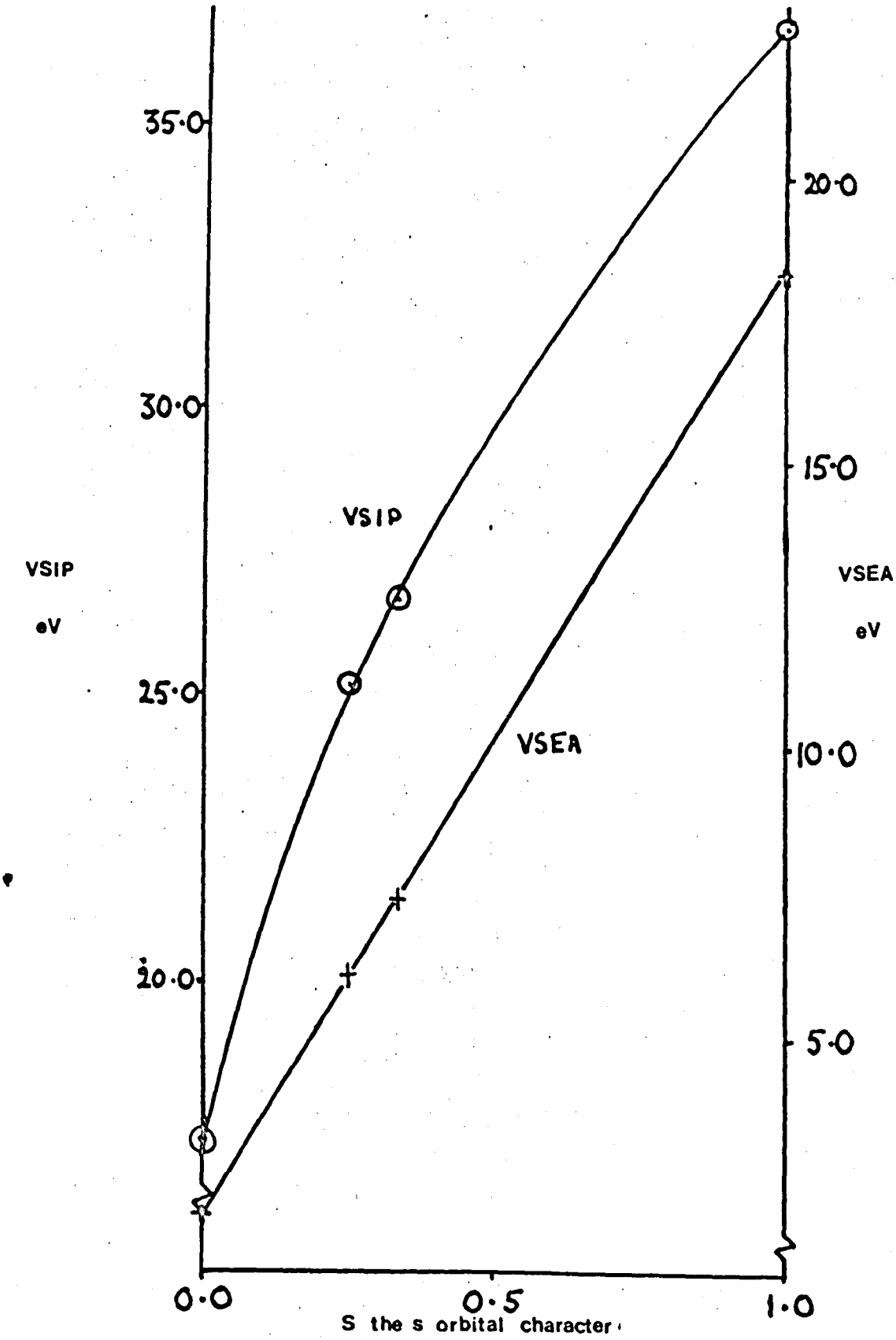


FIGURE 5.1 VARIATION OF VSIP AND VSEA OF OXYGEN VERSUS S, THE S ORBITAL CHARACTER.

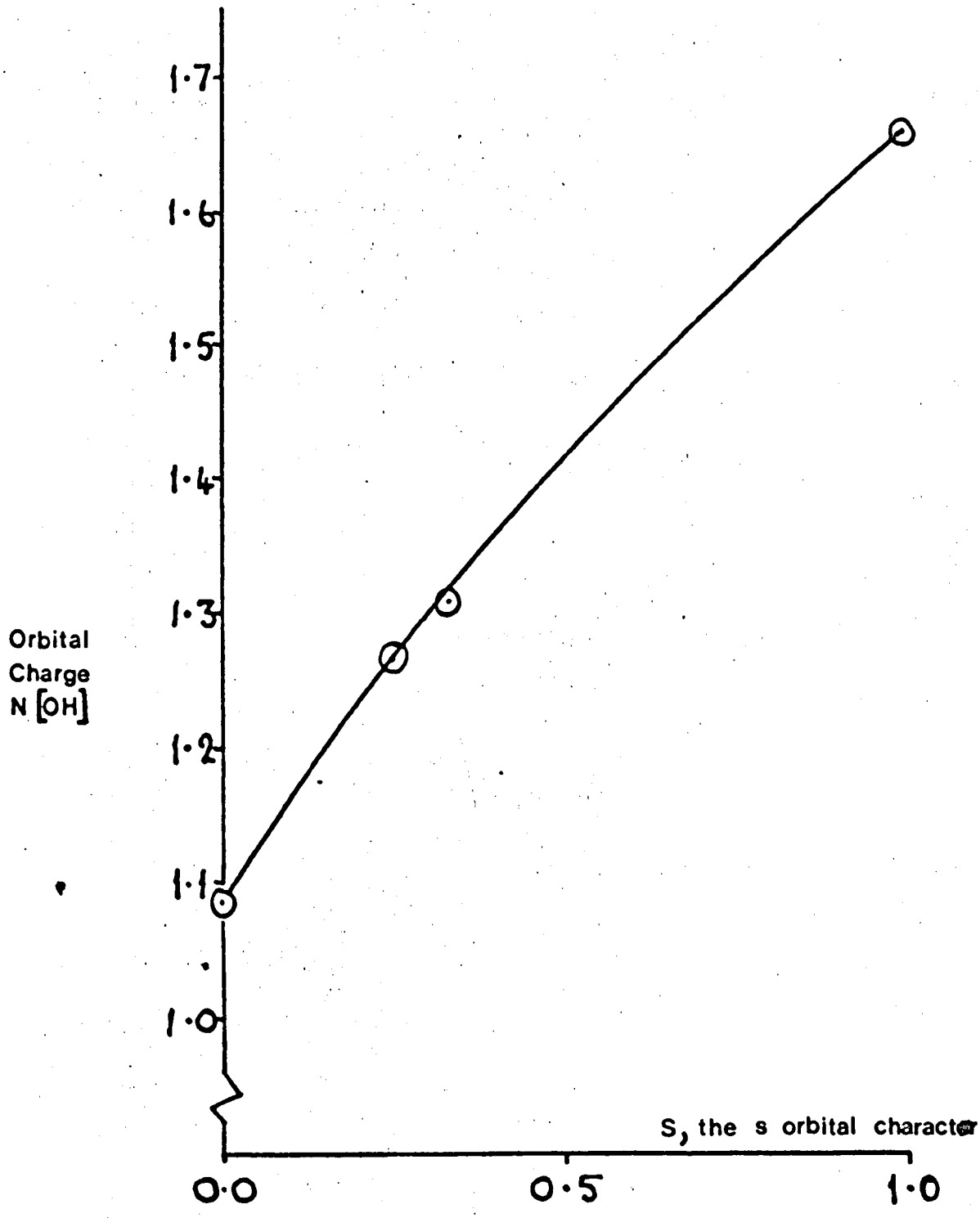


FIGURE 5.2 VARIATION OF ORBITAL CHARGE N[OH] IN AN ISOLATED O–H BOND WITH S, THE S ORBITAL CHARACTER.

$$N(CH) = -k_{OH} (N(OH) + 4) + I_{OH} \qquad (5.1)$$

from which we obtain the expression

$$N(CH) = \frac{(I_{OH} - 4k_{OH})}{(1 + k_{OH})} \qquad (5.2)$$

The parameters k_{OH} and I_{OH} were calculated for three valence states with the hybridisation schemes O (sppp*), S = 0.0; O (tetetete*), S = 0.25; O (tr tr tr* π), S = 0.33; where the asterisk denotes the orbital of interest. The orbital charges, N(OH), in water corresponding to the three valence states were then calculated. The variation of N(OH) in water with S is shown in figure 5.5.

Now it is well known that the hybridisation of oxygen atom in water is neither pure sp3 (te te te te) or pure p (sppp). The measured $\hat{OHO}$ angle in water, θ, is 104.4°. An approximately valid formula relating S to θ[42b] is used to obtain the actual hybridisation of oxygen.

$$S = \frac{\cos \theta}{\cos \theta - 1} \qquad (5.3)$$

Use of this formula gives S= 0.2 for oxygen in water. The value of N(OH) at S = 0.2 from figure 5.3 is 1.17 electrons in good agreement with Peters[33] who obtained the value 1.12 electrons.

In the case of ammonia (figure 5.4) the orbital charge equation is

$$N(NH) = - k_{NH} (2N(NH) + 2) + I_{NH} \qquad (5.4)$$

from which we obtain the orbital charge

$$N(NH) = \frac{(I_{NH} - 2 k_{NH})}{(1 + 2 k_{NH})} \qquad (5.5)$$

The orbital charges, N(NH), were then calculated for ammonia with the central nitrogen atom in the valence states N(sppp*), S = 0.0; N (te te te te*), S = 0.25; N (tr tr tr* π^2), S = 0.33 respectively. These values for N(NH) are plotted against S in figure 5.5.

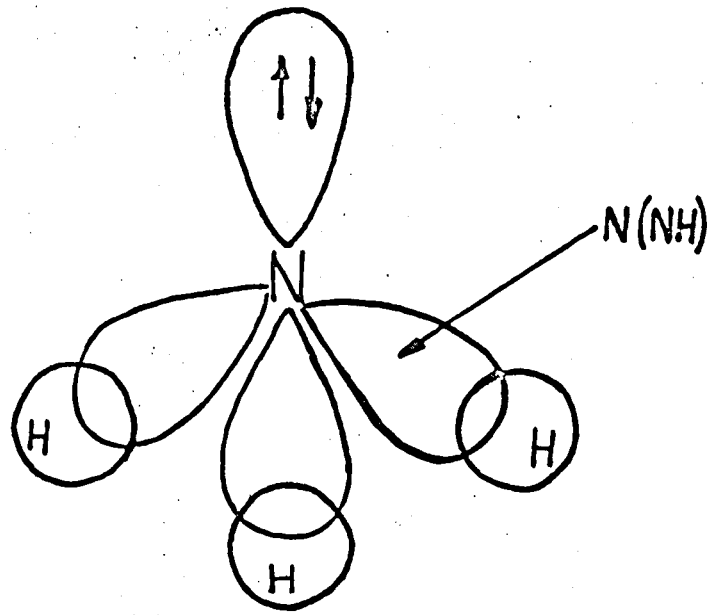


Figure 5·4 Ammonia Molecule.

The $\hat{HNH}$ angle in ammonia, θ, is 106·6°. Using equation 5·3 we obtain the value S = 0·22. The orbital charge, N(NH), corresponding to this S value is 1·09 electrons from figure 5·5. This compares with Peters' value of 1·13 electrons. (Peters' method involves subjecting S.C.F. wavefunctions to unitary transformations to give localised M.O.s which are then analysed).

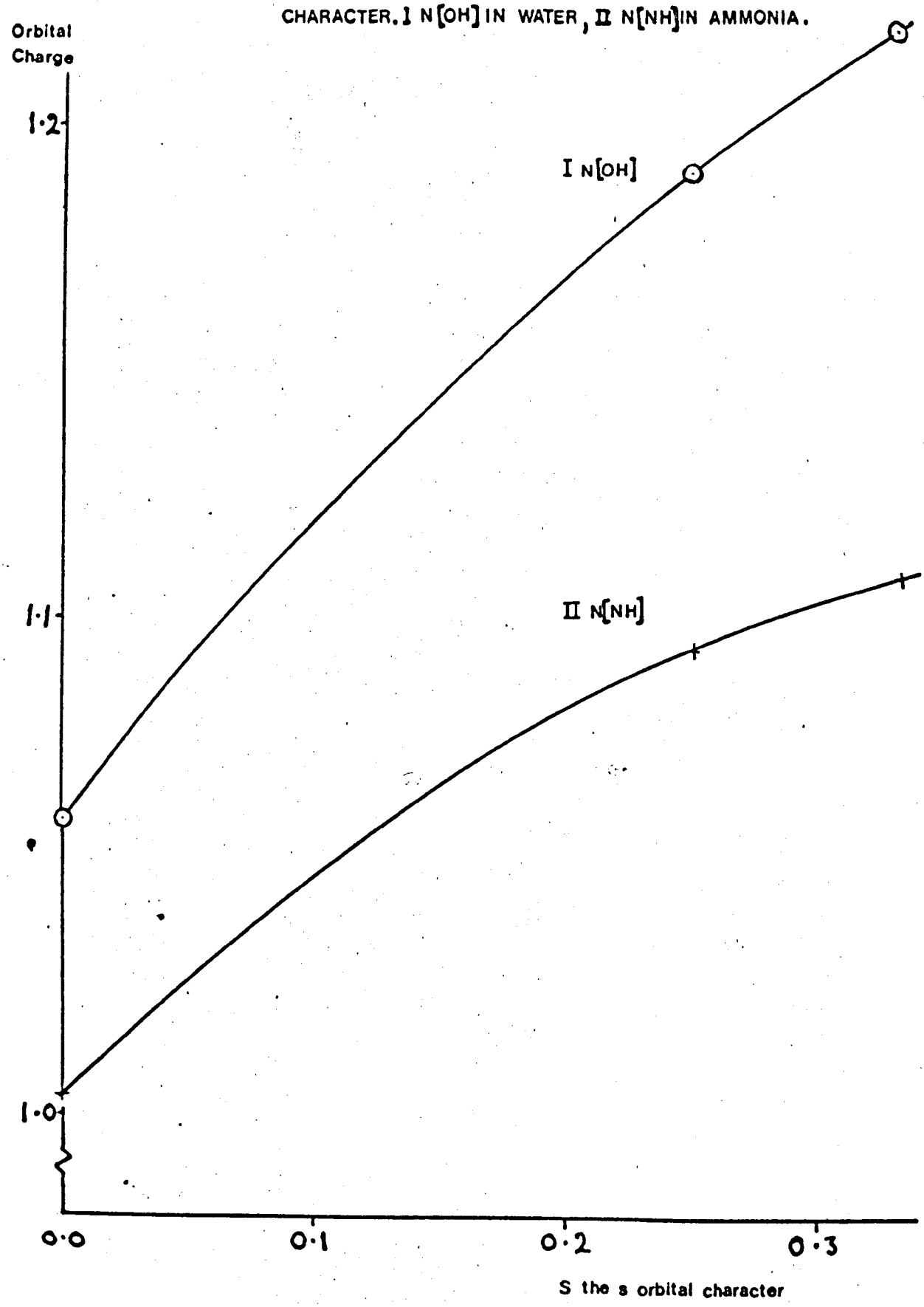
(ii) The HCl and $CH_2C - CHCl_2$ Molecules.

In a study of the HCl molecule, the orbital charges N(ClH) corresponding to values of S, the s orbital character of the chlorine bonding orbital, from 0·0 to 0·5, were calculated. The results are summarised in table 5·1

S	I_{Cl}^{VS}	A_{Cl}^{VS}	N(Cl H)	N(HCl)	i
0·0 (pure p)	15·081	3·725	1·092	0·908	0·092
0·1	16.652	4·796	1·144	0·856	0·144
0·2	18·075	5·871	1·192	0·808	0·192
0·3	19·348	6·944	1·236	0·764	0·236
0·4	20·470	8·016	1·279	0·721	0·279
0·5 (sp hybrid)	21·443	9·087	1·321	0·679	0·321

TABLE 5·1 ORBITAL CHARGES N(Cl H) and other data calculated for the HCl Molecule (i is the ionic character of the H - Cl bond).

FIGURE 5.5 PLOTS OF ORBITAL CHARGE AGAINST S THE S ORBITAL CHARACTER. I N[OH] IN WATER, II N[NH] IN AMMONIA.



Since chlorine (Cl^{35}) has a quadrupolar nucleus the resonance frequency of the chlorine atom in the HCl molecule can be utilised to determine the actual s orbital character, S, of the chlorine bonding orbital. The calculated N(HCl) orbital charges are plotted against S, to obtain the theoretical variation of N(HCl) with S (figure 5·6). On the same graph are also plotted the N(HCl) values obtained from the Townes-Dailey formula[63],

$$\frac{eQ_H}{eQ_A} = N(HCl) \quad (1 - S) \qquad (5.6)$$

against S. (eQ_N^{Cl} = 26·696 M Hzin HCl. eQ_A^{Cl} = 54·873 MHz).

The values of N(HCl) obtained from equation 5·6 are presented in table 5·2.

S	N(HCl)	i
0·0	0·487	0·513
0·1	0·541	0·459
0·2	0·608	0·392
0·3	0·695	0·305
0·4	0·811	0·189
0·5	0·973	0·027

TABLE 5·2 Orbital charges, N(CHI), in HCl calculated from equation 5·6.

The second curve may be regarded as an "experimental" curve. The intersection of the two curves in figure 5·4 gives the values S = 0·343 and N(HCl) = 0·744.

In an earlier piece of work the author studied N.Q.R. frequencies and s orbital characters of C-Cl bonds in a number of chloroparaffins[64]. S values for C-Cl bonds in a molecule in which the chlorine atoms are equivalent are, as one might expect equal. However, in molecules containing two chlorine atoms in different chemical environments the hybrid character of the chlorine bonding orbitals could correspond to

different S values. In the range of molecules presented in table 5·4 of reference [64], the values of S ranged from 0·196 to 0·220.

For the molecule 1,1,2 trichloroethane, $^{(1)}CHCl_2 \cdot {}^{(2)}CH_2Cl$, the orbital charges obtained by calculation when $S_1 = 0.196$ and $S_2 = 0.220$ are

$$N(C_1Cl) = 0.814$$

$$N(C_2Cl) = 0.793$$

When $S_1 = 0.220$ and $S_2 = 0.196$

$$N(C_1Cl) = 0.831$$

$$N(C_2Cl) = 0.810$$

where S_1 represents the amount of s character in the chlorine atoms of the $-CHCl_2$ group and S_2 that for the $-CH_2Cl$ group. Using equation (5·6) one can fix a predicted range for the chlorine atom frequencies.

For Cl ($-CHCl_2$) the predicted frequency range is

$$35.57 < eQq_{Cl} < 37.23 \text{ MHz} \qquad (5.7a)$$

and for Cl ($-CH_2Cl$) the range is

$$33.94 < eQq_{Cl} < 35.74 \text{ MHz} \qquad (5.7b)$$

In an attempt to make a more accurate prediction it was noted that for $CH_2Cl - CH_2Cl$, $S = 0.203$ and for $CHCl_2 - CHCl_2$, $S = 0.199$. Putting $S_1 = 0.199$ and $S_2 = 0.203$ gives the predicted charges.

$$N(C_1Cl) = 0.841$$

$$N(C_2Cl) = 0.804$$

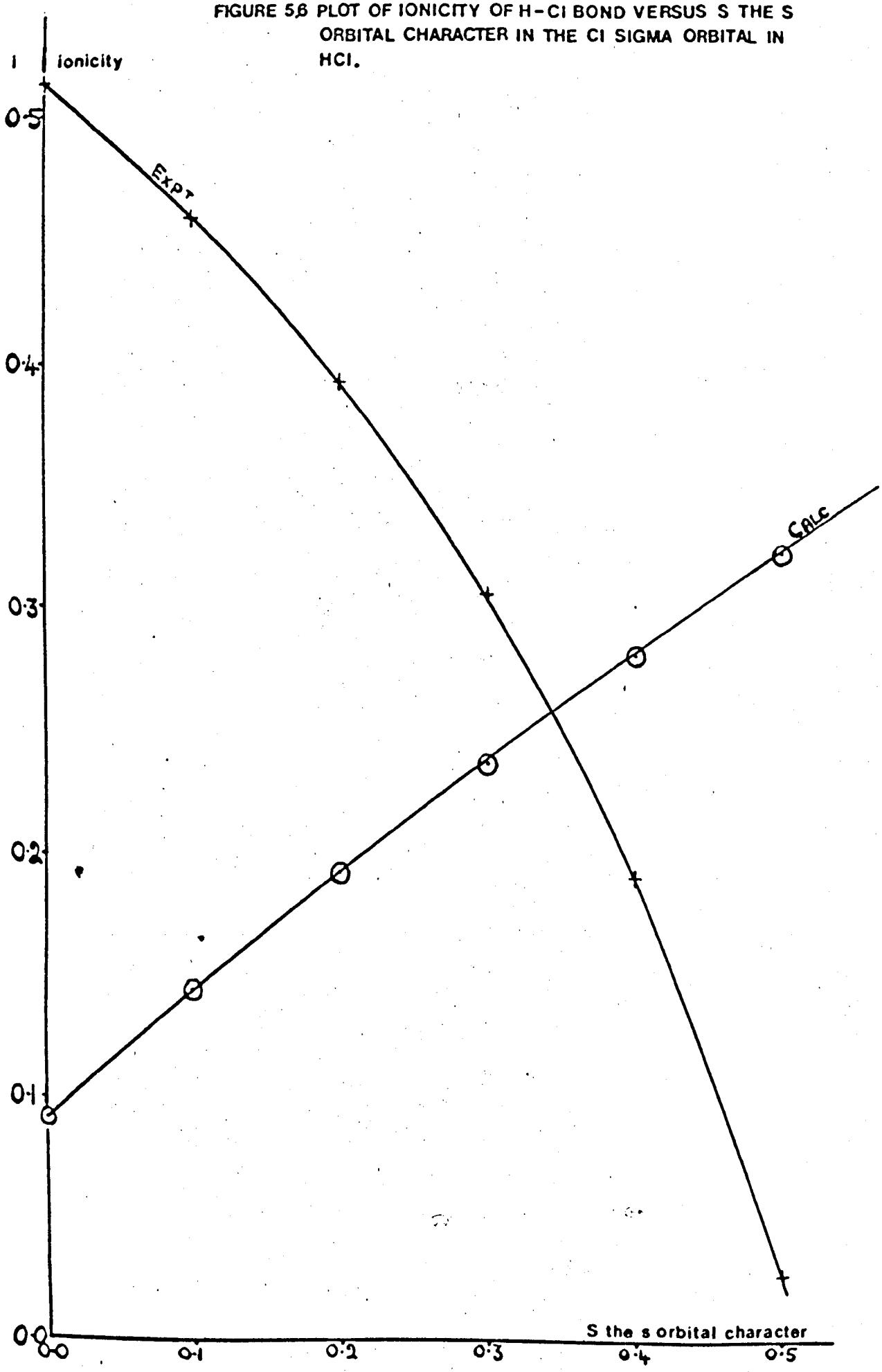
and consequently

$$eQq\ (-CHCl_2) = 36.965 \text{ MHz}$$

$$eQq\ (-CH_2Cl) = 35.162 \text{ MHz}$$

A sample of 1,1,2 trichloroethane was obtained (Ralph N. Emmanuel Ltd.) and N.Q.R. frequency measurements were made in this laboratory (temp. = 77° K, Zeeman modulation frequency 50 cp.s. quench frequency 10 - 25 k Hz).

FIGURE 5.8 PLOT OF IONICITY OF H-Cl BOND VERSUS S THE S ORBITAL CHARACTER IN THE Cl SIGMA ORBITAL IN HCl.



The chlorine atoms in the - $CHCl_2$ group appear to be non-equivalent giving peaks at 36.67 and 36.33 M Hz, while the - CH_2Cl group chlorine atom produces a single peak at 35.30 M Hz. Taking the average of the two - $CHCl_2$ peaks we find experimentally

$$eQq\ (-CHCl_2) = 36.50\ MHz$$

$$eQq\ (-CH_2Cl) = 35.30\ MHz$$

The prediction made for the - CH_2Cl group frequency is therefore satisfactory while that for the - $CHCl_2$ group is less so. However the mid-range value of inequality (5.7a) gives a value of eQq ($-CHCl_2$) of 36.40 MHz.

Prediction of the frequency for the group ($-CHCl_2$) is made difficult by the fact of two Cl frequencies. The equilibrium orbital charges for 1,1,2 trichloroethane are presented in table 5.3.

ORBITAL	CHARGE
$N(C_1Cl)$	0.841
$N(C_1H)$	1.127
$N(C_1C_2)$	1.070
$N(C_2H)$	1.093
$N(C_2Cl)$	0.804

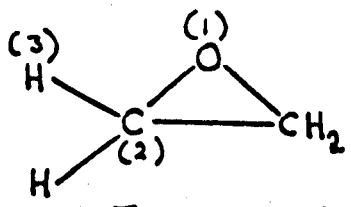
TABLE 5.3 Orbital Charges in 1,1,2 Trichloroethane.

(iii) Charges in ethers

In order to compare the results of our calculations with those of del Re's method[48], which involves a different type of parametrisation, several others were computed. The results are shown in table 5.4, the del Re results are tabulated for comparison.

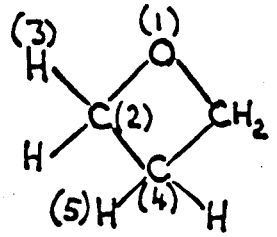
Unfortunately, we do not have any easily obtainable empirical means

of verifying these results.



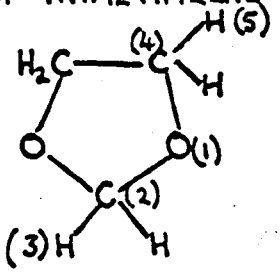
1. ETHYLENE OXIDE

Atom	Net Charge	Net Charge (Del Re)
1	-0.416	-0.274
2	+0.050	+0.034
3	+0.079	+0.052



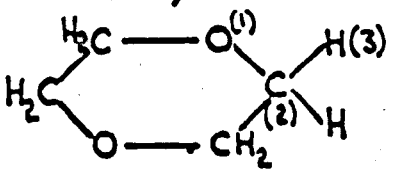
2. TRIMETHYLENE OXIDE

Atom	Net Charge	Net Charge (Del Re)
1	-0.428	-0.278
2	+0.033	+0.023
3	+0.067	+0.050
4	-0.002	-0.051
5	+0.048	+0.041



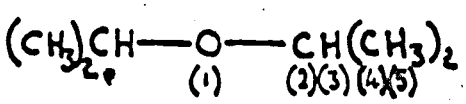
3. 1,3 DIOXALAN

Atom	Net Charge	Net Charge (Del Re)
1	-0.394	-0.259
2	+0.108	+0.117
3	+0.114	+0.062
4	+0.058	+0.035
5	+0.084	+0.052



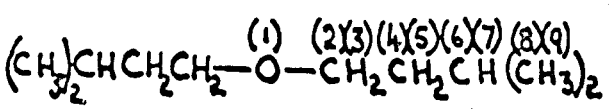
4. 1,4 DIOXAN

Atom	Net Charge	Net Charge (Del Re)
1	-0.416	-0.289
2	+0.150	+0.070
3	+0.079	+0.038



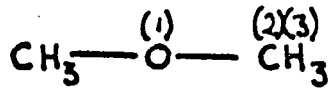
5. DI-ISOPROPYL ETHER.

Atom	Net Charge	Net Charge (Del Re)
1	-0.434	-0.284
2	+0.020	+0.069
3	+0.061	+0.048
4	-0.028	-0.108
5	+0.032	+0.040



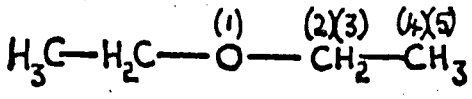
6. DI-ISOAMLYL ETHER.

Atom	Net Charge	Net Charge (Del Re)
1	-0.432	-0.278
2	+0.023	+0.022
3	+0.063	+0.050
4	-0.023	-0.063
5	+0.035	+0.039
6	-0.037	-0.028
7	+0.027	+0.037
8	-0.048	-0.118
9	+0.021	+0.039



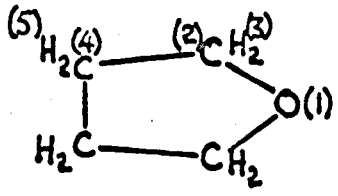
8. DIMETHYL ETHER.

Atom	Net Charge	Net Charge (Del Re)
1	-0.431	-0.272
2	+0.024	-0.023
3	+0.064	+0.053



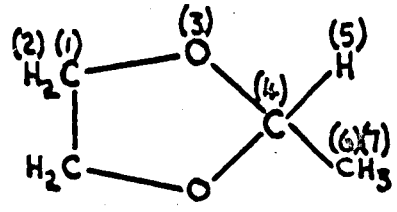
9. DIETHYL ETHER.

Atom	Net Charge	Net Charge (Del Re)
1	-0.433	-0.280
2	+0.022	+0.050
3	+0.062	+0.024
4	-0.028	-0.105
5	+0.033	+0.040



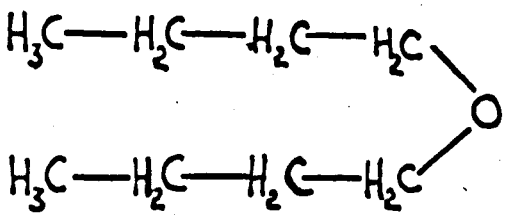
10. TETRAHYDROFURAN.

Atom	Net Charge	Net Charge (Del Re)
1	-0.431	-0.282
2	+0.026	+0.023
3	+0.064	+0.050
4	-0.017	-0.060
5	+0.039	+0.039



11. 2-METHYL DIOXALAN.

Atom	Net Charge	Net Charge (Del Re)
1	+0.057	+0.120
2	+0.083	+0.051
3	-0.398	-0.413
4	+0.098	+0.263
5	+0.108	+0.070
6	0.0	-0.071
7	+0.048	+0.040



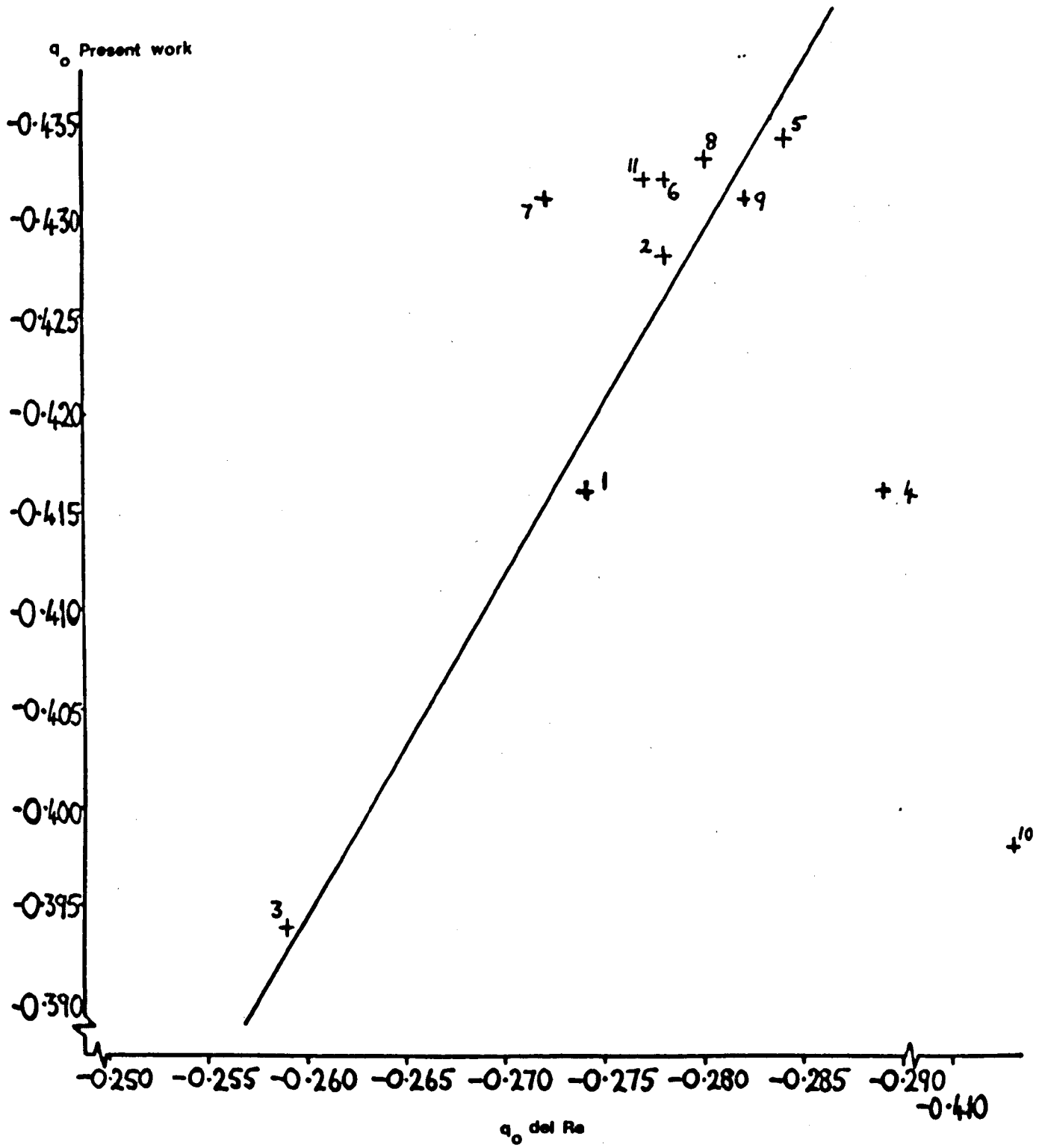
7. n-BUTYL ETHER.

Atom	Net Charge	Net Charge (Del Re)
1	-0.432	-0.277
2	+0.022	+0.019
3	+0.063	+0.050
4	-0.025	-0.062
5	+0.035	+0.039
6	-0.039	-0.072
7	+0.025	+0.038
8	-0.048	-0.118
9	+0.020	+0.039

TABLE 5.4 Net sigma charges in ethers.

Within individual molecules similar qualitative features of the charge distribution are found in the calculated results. Thus the oxygen atom is a strong attractor of charge and sets up strong inductive effects via the adjacent C-O bonds. For example in trimethylene oxide the polarity of the $C_{(2)}$-$O_{(1)}$ bond is 0·214 electrons towards the oxygen while the polarity of the C-C bond is 0·047 electrons. The polarity of any bond falls as the number of bonds between it and the oxygen atom increases. Thus in n butyl ether the polarity of the bonds is in the order 0·216 (C-O), 0·068, 0·023, 0·012 ($C_{(6)}$-$C_{(8)}$), electrons where the polarity is towards oxygen in the C-O bond and is towards the end of the bond nearest the oxygen atom in each of the C-C bonds. In figure 5·7 the two sets of charges (on the O atom) are shown graphically.

FIGURE 5.7 NET SIGMA CHARGES ON OXYGEN IN ETHERS.



Up to and including molecule 7 the change in charge on the oxygen atom follows roughly the same pattern in both methods. The high charge on the oxygen, in molecule 11, as calculated be del Re's method seems to be out of line with other charges computed by that method.

(iv) Relations with E.S.C.A. (Electron Spectroscopy for Chemical Analysis.

Electron spectroscopy is a field of study which began some years ago but owing to poor resolution of spectra was little appreciated as a means of chemical analysis until quite recently. A large number of articles on the subject have appeared in the literature in recent years covering a wide range of topics of chemical interest[65-69].

The basis of the technique is the high resolution of the energy distribution obtained when electrons are expelled from their orbitals in molecules. Depending on the energy of the incident radiation, valence shell or inner shell electrons can be excited[70]. The electrons emitted may be photoelectrons or Auger electrons[71]. (In an Auger process one electron drops down into the hole left by the excitation while one electron goes off into the continuum. The latter electron carries away a discrete amount of energy equal to the energy difference between the initial and final states).

Since the energy of the photoelectrons is equal to the energy of the incident photons minus the binding energy,

$$E = h\nu - E_b \qquad (5\cdot8)$$

the electronic energy levels of the sample can be determined directly (71, 75).

There are two main ways in which electron spectroscopy is used to provide information about chemical structure.

First of all it may provide information about chemical bonding. The chemical environments of atoms in molecules leads to the atoms bearing

non-neutral charges. In electron spectroscopy the individual atoms are regarded as spheres with different potentials, the potentials being determined by the chemical environment. This atomic potential gives rise to inner shell binding energies being shifted by a definite amount, compared to the binding energy in the neutral atoms. The changes in atomic potential reflect the nature of the chemical bonds formed by the atom, and implicitly the valence electron structure. Such "chemical shifts" have been measuredfor a number of molecules.

The second main area of interest connected with electron spectroscopy is that of molecular ionisation potentials and electronic energy levels. Since electronic energies are obtained experimentally it should, in principle, be possible to identify the energies of the electrons departing from the various M.O.s in the molecule. Clearly the order in which the electrons "come off" the molecule is going to be important. Identifying the energies of emerging photoelectrons with definite M.O.s depends on

(a) the validity of Koopman's theorem, on which the interpretation is based, and
(b) reliable theoretical methods for calculating the eigenvalues and eigenvectors of the molecular Hamiltonian.

We have to assume (a) is valid but (b) is very important. In this respect all valence electron methods are preferable to π electron only methods for obvious reasons. The extended Hückel method has been used with some success[73]. On the whole no method has been found to be reliable enough and currently considerable energy is being applied to developing a method suitable for accurate correlation of theory with practice.

E.S.C.A., of all areas of practical chemistry, is possibly the one which provides the most direct contact with fundamental chemical features of atoms and molecules. The theoretical method outlined

in this thesis is not aimed directly at finding the energy levels of saturated systems, or even for σ type energy levels in non-saturated molecules.

However, it can be used in conjunction with E.S.C.A. to investigate the chemical structure of simple systems. As has already been stated, the chemical environment of a molecule closely affects the binding energy of the core electrons. One relation which links the chemical shift ΔE_i of an atom i, in a molecule, with the charges on the atoms in molecules is[72]

$$\Delta E_i = kq_i + V_i + \ell \qquad (5.9)$$

where

$$V_i = \sum_{j \neq i} \frac{q_j}{R_{ij}}$$

(the molecular potential at nucleus i)

and q_i is the charge on atom i, R_{ij} is the distance between atoms i and j, k is a constant which depends on the element, ℓ is a constant which depends on the choice of energy level. Relations like this have already been employed with some success[70, 73, 76, 77]. Basch and Snyder[77] obtained acceptable linear plots of ΔE_i against q_i for molecules containing C, N, O and F atoms. In this work the V_i term was neglected. This presumably indicates that either the core binding energies are determined almost entirely by the electronic charge on the atom concerned or that the V_i term is similar in sign & magnitude in the molecules studied.

In table 5·5 are presented values of ΔE_{1s} (exp), the carbon core 1s binding energy and q_c, the net electronic charge on the carbon atom as calculated by the method described in this thesis, for a number of molecules.

Molecule	ΔE_{1s} (exp)*	q_c
CH_3F	2.8[a]	+0.081
CH_2F_2	5.6[b]	+0.226
CHF_3	8.3[a]	+0.382
CF_4	11.0[a]	+0.544
CH	1.6[a]	+0.025
CH_3Cl	3.1[a]	+0.110
CH_2Cl_2	4.3[a]	+0.186
CCl_4	5.5[a]	+0.260
$*CH_3CH_2OH$	0.2[b]	-0.025
$CH_3{}^*CH_2CH$	1.6[b]	+0.030
CH_3CH	1.6[b]	+0.033
$CH_2CH_2CH_2$	0.5[c]	-0.044
C_2H_6	-0.2[b]	-0.053
C_2H_4	0.1	-0.090
C_2H_2	0.4[b]	-0.119

a ref (65)
b ref (72)
c ref (77)

Energies are in eV.
* relative to CH_4

TABLE 5.5 Core 1s Binding Energies and net charges on carbon.

A plot of binding energies against net electronic charge on carbon is shown in figure 5·8. The equation of the line is

$$\Delta E_{1s} = 17{\cdot}544\, q_c + 1{\cdot}285 \qquad (5{\cdot}10)$$

One feature of these results is that the last three molecules in table 5·5, i.e. C_2H_6, C_2H_4 and C_2H_2 do not seem to fall in line with the other molecules. The results suggest, in fact, that the binding energy for these three molecules increases with increasing charge. To investigate this the ΔE's for these molecules have been plotted against the corresponding q's. (see figure 5·8). The graph appears as a straight line of slope roughly opposite to that of the line in figure 5·8. It must of course be borne in mind that the values involved are very small and the correspondence may be a fortuitous one. If the last three molecules are left out of the analysis the equation of the line is

$$\Delta E_{1s} = 18{\cdot}426\, q_c + 1{\cdot}065 \qquad (5{\cdot}11)$$

Linear relationships like (5·10) and (5·11) could be used to predict the binding energies in molecules not yet investigated by E.S.C.A.

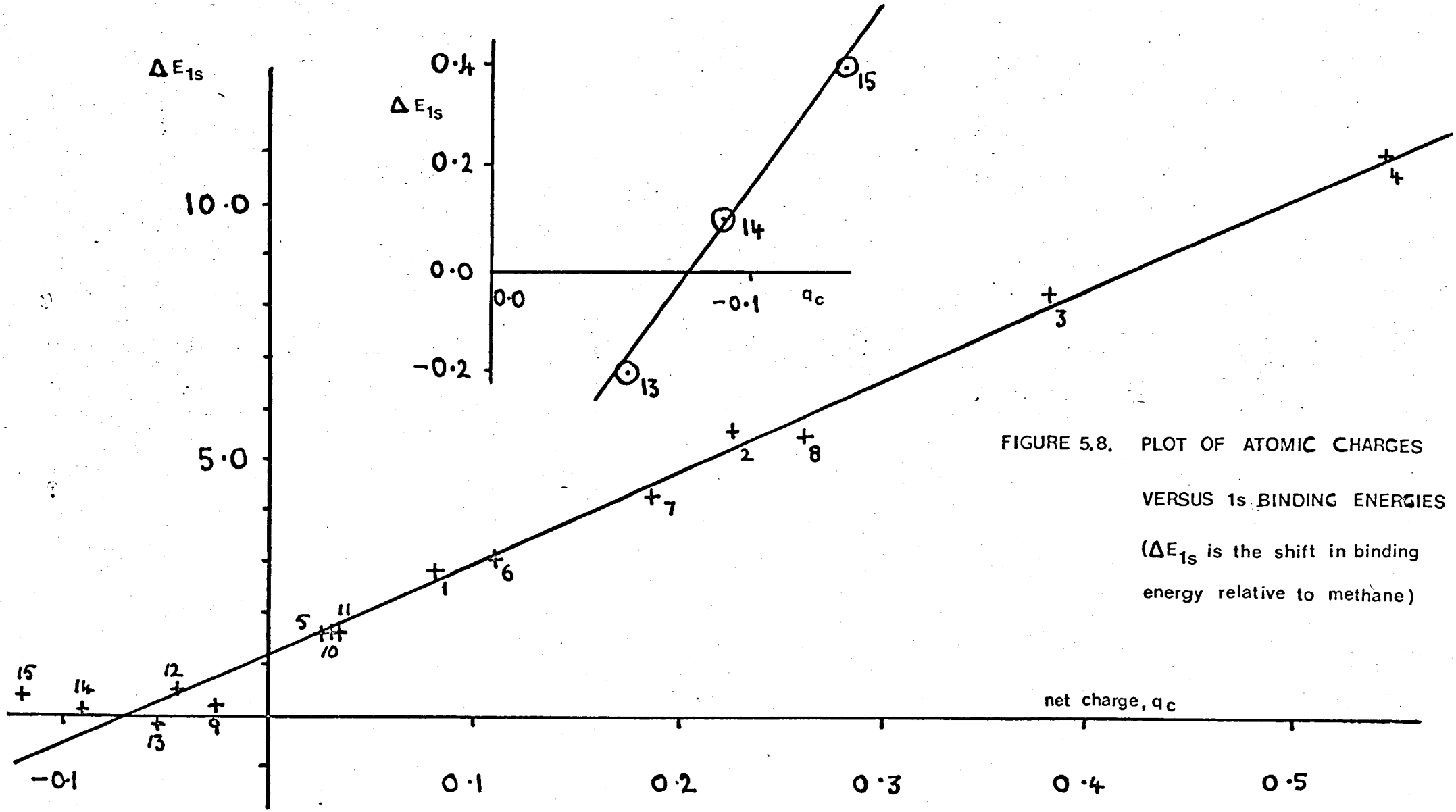


FIGURE 5.8. PLOT OF ATOMIC CHARGES VERSUS 1s BINDING ENERGIES (ΔE_{1s} is the shift in binding energy relative to methane)

Chapter 6

Preliminary efforts at developing a ($\sigma-\pi$) electron approach.

(i) Introduction

The development of molecular orbital methods for the computation of various properties of molecules can be grouped into 6 main types. These are by no means mutually exclusive and several intermediate methods may well have been used or are being used. The 6 main groups are

1. π electron or σ electron only calculations
   e.g. H.M.O. (π) [78] Sandorfy's and Fukui's H.M.O. (σ), [79-82] Sandorfy's P.P.P. (σ) [83], P.P.P. (π) [84,59]
2. π and σ distributions computed separately and effects combined to give approximate full treatment. [85]
3. σ calculation is performed first to provide a perturbed potential framework for a subsequent π electron calculation e.g. V.E.S.C.F. method [88], Momicchioli and del Re's P.P.P. method [89]. In the latter calculation, σ electron effects are brought in as a constant additive term to the diagonal elements on each cycle of a P.P.P. method.
4. Iterative $\sigma-\pi$ calculations such as the BEEM - π method of Whitehead et al [90-92].
5. All valence electron calculations CNDO [93], INDO [94], etc.
6. All electron ab initio methods [95,96,135]

Historically, the direction of theoretical chemistry was from simple Hückel methods through the Pariser - Parr-Pople and related schemes to the all valence electron calculations. AB initio calculations, previously hampered because of the store and speed limitations of computers have recently shown rapid acceleration. Clementi and co-workers have done

much good work in this field[95].

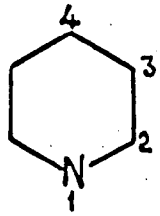
Lykos has suggested the possibility that due to the symmetry of the "core" and the "peel"[3], a sigma electron calculation could be carried out and the resulting eigenvectors could be used to build $\sigma - \pi$ Coulomb operators for inclusion in a pi Hamiltonian. The latter is then caused to operate on a pi only wave function and the resulting eigenvectors are then used to build a sigma Hamiltonian, and so on until self consistency. Of course a complete treatment of this sort would only be a little less involved than a full S.C.F. calculation, and it could conceivably be more involved.

(ii) A possible method.

At a rather lower level of approximation one could neglect only those $\sigma - \pi$ interactions which are small in magnitude. This essentially reduces to performing an approximate sigma calculation and linking it to an approximate π calculation. One is then faced with a choice of methods. Whitehead and co-workers used their bond electonegativity equalisation method (B.E.E.M.) for the sigma part of the calculation in conjunction with simple H.M.O. theory[90-92]. This method was called by them B.E.E.M. - π

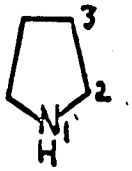
A similar scheme was followed by the present author, although the sigma electron calculation used was rather more concise. The results given elsewhere are summarised in the following examples. The method is known as the iterative self consistent charge method (I.S.C.C.M.).

PYRIDINE



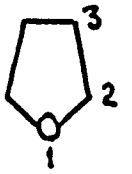
	1	2	3	4
π	+0·022	−0·029	+0·014	+0·006
σ	−0·304	+0·024	−0·049	−0·049
$(\sigma+\pi)$	−0·282	−0·005	−0·035	−0·043

PYRROLE



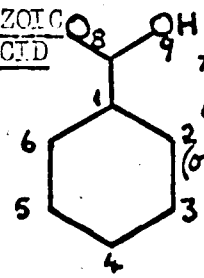
	1	2	3
π	+0·421	−0·103	−0·108
σ	−0·616	+0·072	+0·022
$(\sigma+\pi)$	−0·195	−0·031	−0·086

FURAN



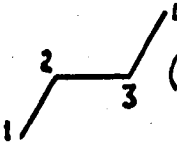
	1	2	3
π	−0·746	+0·152	+0·037
σ	+0·407	−0·116	−0·086
$(\sigma+\pi)$	−0·339	+0·036	−0·049

BENZOIC ACID



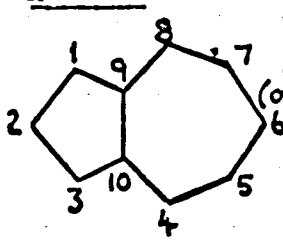
	1	2	3	4	7	8	9
π	+0·119	+0·008	+0·010	−0·015	−0·062	−0·031	+0·082
σ	−0·065	−0·052	−0·037	+0·069	+0·214	−0·266	−0·444
$(\sigma+\pi)$	−0·046	−0·044	−0·027	+0·024	+0·182	−0·297	−0·362

BUTADIENE



	1	2
π	+0·007	−0·007
σ	−0·088	−0·065
$(\sigma+\pi)$	−0·081	−0·072

AZULENE



	1	2	4	5	6	9
π	−0·135	−0·029	+0·121	+0·008	+0·104	−0·031
σ	+0·034	−0·064	−0·141	−0·041	−0·122	−0·021
$(\sigma+\pi)$	−0·101	−0·093	−0·020	−0·033	−0·018	−0·052

FIGURE 6·1 Sample results of I.S.C.C.M. computation.

Briefly, the method is as follows. A uniform π charge distribution is assumed initially and the σ charge distribution is then computed. The one centre core integrals - the Coulomb integrals - are treated as functions of the electron occupancy at the particular atom, X, in the core by the relation

$$\alpha_x = \alpha_c + h_x \beta_{cc} \qquad (6.1)$$

where α_c is the Coulomb integral of a neutral trigonally hybridised carbon atom, β_{cc} is a resonance integral and h_x is an inductive parameter which varies with the charge on atom X as follows.

$$h_x = A + Bq_x + Cq_x^2 \qquad (6.2)$$

q_x is the net σ charge on atom X and A,B,C are coefficients constant for the particular atom X, and which depend, also on the valence state of atom X.

(iii) Charge-dependent inductive parameters - some problems.

The expression 6.2 is derived from the relation[102]

$$h_x = \frac{-(I_x + \frac{1}{2}\eta_x J_{xx}) - (-I_c - \frac{1}{2} J_{cc})}{4.23} \qquad (6.3)$$

Usually in simple H.M.O. work h is given a definite value which reproduces, it is hoped, the π electron properties obtained in more sophisticated calculations. Streitweiser[98], Kier[99] and Pullman[100] all give lists of typical values.

Now h_x should be of such a magnitude that $\alpha_c + h_x \beta_{cc}$ is about equal to F_{xx} the diagonal matrix element appearing in the Hamiltonian in P.P.P. or similar methods. For example, in Pyridine F_{nn} is about - 6ev, and if we assume that $\alpha_c = -\frac{1}{2}(I_c - A_c) = -5.6$ eV and $\beta_{cc} = -2.4$ eV then h_n would have to have a value of at least 0.1 in order for α_n to approximate F_{nn}.

Brown and Heffernan have suggested a value for h_n of 0.176[86] as being necessary to reproduce, by an H.M.O. method, the features of a V.E.S.C.F. calculation on Pyridine. In conventional H.M.O. theory h_n is frequently given the value 0.5[101, 110].

From the work of Baird and Whitehead[102], the reason why simple H.M.O. methods give π charge distribution similar to those of P.P.P. methods is apparent. Unfortunately, however, when h_X is rendered charge dependent through equation (6·2) and (6·3) a paradox arises in the case of Pyridine. In the particular case of the Pyridine nitrogen atom the equation for h_n is

$$h_n = 0{\cdot}56 + 2{\cdot}43\, q_n + 0{\cdot}49 q_n^2 \qquad (6{\cdot}4)$$

It is certainly true that H.M.O. methods which use a value of 0·5 for h_n give a π electron distribution which is similar to that given by a P.P.P. calculation.

However, the only way in which a value of 0·5 can be obtained from equation (6·4) is if $q_x = 0{\cdot}0$ i.e. it assumes a net sigma charge on the nitrogen atom of zero. This seems wrong in the first place because the C - N sigma bonds are generally regarded as having a polarity towards the nitrogen atom[103].

If equation (6·4) is used in the calculation then nonsensical results are obtained in the iterative solution of the secular equations. This arises because assuming initially unit π charges, a calculation of sigma charges leads to a net negative sigma charge on the nitrogen atom so that on the first cycle of the H.M.O. calculation a π charge of less than unity is obtained on that atom. A second sigma calculation using the new π charges leads to an even larger polarisation of the sigma electrons in the C - N bonds towards the nitrogen atom so that on the next cycle of the H.M.O. calculation an even smaller π charge is produced on the nitrogen atom. Eventually the nitrogen atom bears a large sigma charge and a small pi charge.

This problem can be partially overcome by using net $(\sigma + \pi)$ charges in equation (6·4) instead of net σ charges. This means that prior to the nth cycle of the H.M.O. calculation the nth sigma charges and the nth - 1

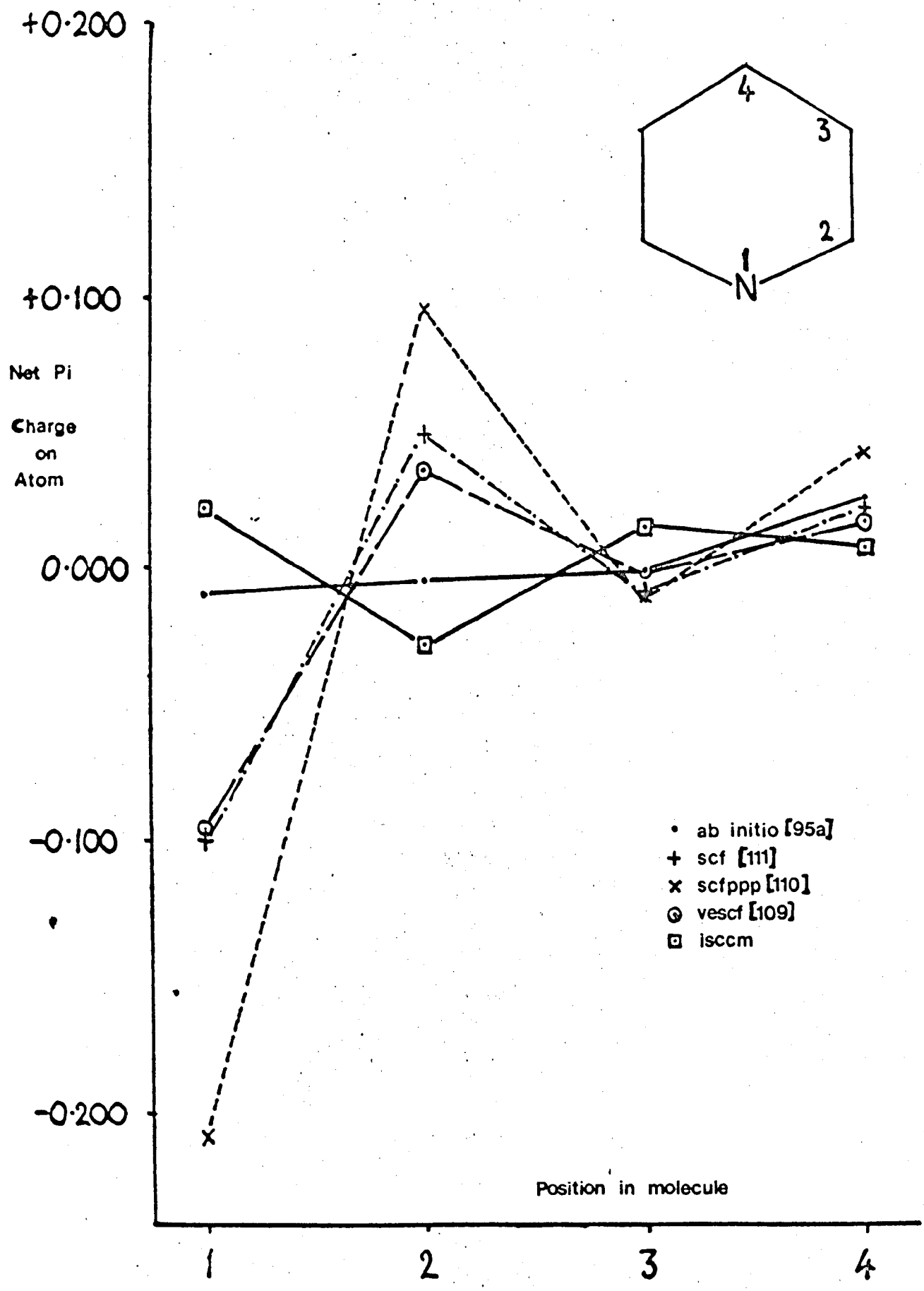


FIGURE 6.2. NET PI CHARGES IN PYRIDINE – VARIOUS METHODS.

pi charges are added together to give a net total charge. It need hardly be said that this is an ad hoc modification and is therefore unsatisfactory from a theoretical point of view, although it does not in fact contradict Slater's rules whereby all the electrons in the valence shell of an atom shield each other to an equal extent.

From the results given in table 6·1, one can see that the pyridine type nitrogen atom has a π charge of less than unity, which is in striking contrast to most other methods. (see the charge profile in figure 6·2). Whitehead has found a similar situation with regard to pyridine using B.E.E.M. - π [5].

In Pyrrole and Furan the charges obtained using I.S.C.C.M. are comparable to the charges resulting from other calculations. Some representative results for Pyrrole are presented in table 6·1.

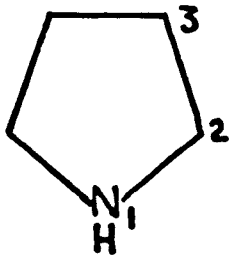
The most important variable parameter in methods which link the sigma and pi electronic distributions by means of inductive effects is h_x. The h_n values for Pyridine type nitrogen atoms in the above calculation is low ..... and if the pi charge distribution is to be improved it can only be done by increasing h_n.

(iv) An attempted improvement in I.S.C.C.M.

Two possible reasons for the low h_n values suggest themselves.

(i) Delocalisation of the lone pair electrons,
(ii) The sigma charge drifts, towards the nitrogen atom, in the C-N bonds are too large. (in pyridine the sigma charge transfer is 0·159 electrons towards nitrogen in each bond).

ATOM	MINDO/2 (104)			CNDO/2 (105)			VESCF (106)	ab initio (107)			SCFPP (108)
	σ	π	σ+π	σ	π	σ+π	π	σ	π	σ+π	π
1	-0·658	+0·289	-0·359	-0·563	+0·345	-0·218	+0·281	-0·749	+0·341	-0·408	+0·225
2	+0·064	-0·102	-0·038	-0·003	-0·085	-0·088	-0·070	-0·030	-0·075	-0·105	-0·061
3	+0·226	-0·043	+0·182	+0·162	-0·085	+0·077	-0·071	-0·160	-0·096	-0·256	-0·052



ATOM	ISCCM		
	σ	π	σ+π
1	-0·616	+0·421	-0·195
2	+0·072	-0·103	-0·031
3	+0·022	-0·108	-0·086

TABLE 6·1 ELECTRONIC CHARGES IN PYRROLE

To deal with point (i) first. In I.S.C.C.M. we neglect completely the effect of lone pairs lying in the plane of the molecule. It is assumed that the lone pair contains two localised electrons. In an approximate theory like I.S.C.C.M. any attempt to deal with lone pairs would be an unjustifiable sophistication. Consequently any lone pair effects will continue to be neglected.

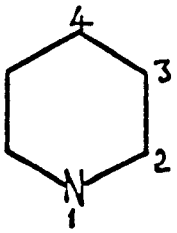
Regarding the second point, an attempt was made to alter the magnitudes of the sigma charge drifts without altering their qualitative features. This was done in the following manner. The functional form of the expression used in calculating the charges in the parametrisation scheme is

$$N(AB) = \frac{4\,(I_A - I_B) - K\,(I_A + A_A - I_B - A_B)}{2\,(I_A + I_B - A_A - A_B)} \qquad (6.4)$$

When K = 1·0, equation (6.4) becomes the completely correlated expression 3·14, and when K = 0·0 it becomes the non-correlated expression 3·50. Noting that sigma parameters computed using the latter expression gave much larger sigma charge transfers than those obtained from the former one, a possible investigation could be based on a series of parameters calculated using K = 1·0 up to K = 1·6. There is admittedly an element of artificiality here, but the basic equations themselves are only approximate. It was therefore, decided that this process might provide some idea of the effects of parameters of various magnitudes. The results for several molecules are now presented.

(v) Results of Preliminary investigation of sigma charge parameters.

The results for the Pyridine molecule are presented in table 6.2.



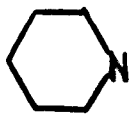
$\beta_{CN} = \beta_{CC}$

		ATOM				
		1	2	3	4	h_N
K = 1·0	π	+0·022	-0·029	+0·014	+0·006	
	σ	-0·304	+0·024	-0·049	-0·049	-0·087
	$(\sigma+\pi)$	-0·282	-0·005	-0·035	-0·043	
K = 1·1	π	+0·004	-0·022	+0·015	+0·010	
	σ	-0·260	+0·022	-0·046	-0·049	-0·030
	$(\sigma+\pi)$	-0·256	-0·000	-0·031	-0·039	
K = 1·2	π	-0·013	-0·015	+0·015	+0·013	
	σ	-0·219	+0·019	-0·042	-0·046	+0·023
	$(\sigma+\pi)$	-0·232	+0·004	-0·027	-0·033	
K = 1·3	π	-0·028	-0·009	+0·015	+0·016	
	σ	-0·172	+0·017	-0·037	-0·043	+0·070
	$(\sigma+\pi)$	-0·210	+0·008	-0·022	-0·027	
K = 1·4	π	-0·042	-0·002	+0·015	+0·018	
	σ	-0·148	+0·013	-0·033	-0·039	+0·115
	$(\sigma+\pi)$	-0·190	+0·011	-0·018	-0·021	
K = 1.5	π	-0·054	+0·003	+0·014	+0·019	
	σ	-0·118	+0·012	-0·027	-0·033	+0·156
	$(\sigma+\pi)$	-0·172	+0·015	-0·013	-0·014	
K = 1·6	π	-0·065	+0·009	+0·014	+0·020	
	σ	-0·091	+0·009	-0·022	-0·027	+0·193
	$(\sigma+\pi)$	-0·156	+0·018	-0·008	-0·007	

TABLE 6·2 Effect of varying sigma bond parameters on charge distribution in Pyridine.

The dipole moments calculated using the point charge approximation are

presented in table 6·3.

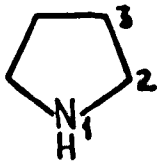


Calculation	Dipole Moments (Debyes)		
	μ_σ	μ_π	$\mu_{\sigma+\pi+lp}$
K = 1·0	1·858	0·167	3·796
K = 1·1	1·531	0·288	3·589
K = 1·2	1·263	0·375	3·408
K = 1·3	1·018	0·455	3·243
K = 1·4	0·802	0·529	3·101
K = 1·5	0·619	0·556	2·975
K = 1·6	0·489	0·609	2·868

exp = 2·25 D (116)

TABLE 6·3 CALCULATED DIPOLE MOMENTS IN PYRIDINE (μ_{lp} = 1·77 D)

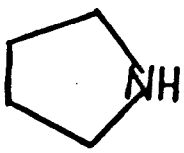
The calculated charge distributions in pyrrole are presented in table 6·4.



		ATOM 1	2	3	h_N
K = 1·0	π	+0·421	-0·103	-0·108	
	σ	-0·616	+0·072	+0·022	0·946
	$(\sigma+\pi)$	-0·195	-0·031	-0·086	
K = 1·3	π	+0.347	-0.085	-0.089	
	σ	-0.422	+0.061	+0.003	1.282
	$(\sigma+\pi)$	-0.075	-0.024	-0.086	
K = 1·6	π	+0·286	-0·065	-0·078	
	σ	-0·243	-0·041	-0·003	1·628
	$(\sigma+\pi)$	+0·043	-0·024	-0·081	

TABLE 6·4 COMPUTED CHARGES IN PYRROLE FOR VARIOUS SIGMA BOND PARAMETERS.

The calculated dipole moments in pyrrole are shown in table 6·5.

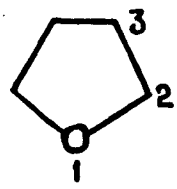


CALCULATION	DIPOLE MOMENTS (Debyes)		
	μ_σ	μ_π	$\mu_{\sigma+\pi}$
K = 1·0	1·875 →	3·023 ←	1·148 ←
K = 1·1	1·471 →	2·812 ←	1·341 ←
K = 1·2	1·130 →	2·642 ←	1·512 ←
K = 1·3	0·901 →	1·422 ←	1·590 ←
K = 1·4	0·695 →	2·363 ←	1·667 ←
K = 1·5	0·532 →	2·225 ←	1·693 ←
K = 1·6	0·385 →	2·108 ←	1·723 ←

μ_{exp} = 1·84 D (103)

TABLE 6·5 CALCULATED DIPOLE MOMENTS IN PYRROLE.

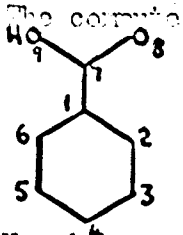
The calculated electronic charges in furan are presented in table 6·6.



		ATOM 1	2	3
K = 1·0	σ	−0·746	+0·152	+0·037
	π	+0·407	−0·116	−0·086
	$(\sigma+\pi)$	−0.339	+0·036	−0·049
K = 1·2	σ	−0·558	+0·136	+0·014
	π	+0·329	−0·098	−0·067
	$(\sigma+\pi)$	−0·229	+0·038	−0·053
K = 1·4	σ	−0·401	+0·912	0·000
	π	+0.271	−0·080	−0·055
	$(\sigma+\pi)$	−0·130	+0·032	−0·055
K = 1·6	σ	−0·260	+0·083	−0·004
	π	+0·225	−0·062	−0·051
	$(\sigma+\pi)$	−0·035	+0·021	−0·055

TABLE 6·6 COMPUTED CHARGES IN FURAN FOR VARIOUS SIGMA BOND PARAMETERS.

The computed electronic charges in benzoic acid are shown in table 6.7.

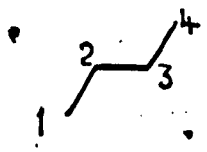


		ATOM						
		1	2	3	4	7	8	9
K = 1.0	π	+0.019	+0.008	+0.010	-0.045	-0.062	-0.031	+0.082
h_{O8} = +0.061	σ	-0.055	-0.062	-0.037	+0.069	+0.244	-0.266	-0.444
h_{O9} = +1.046	$(\sigma+\pi)$	-0.046	-0.044	-0.027	+0.024	+0.182	-0.297	-0.362
K = 1.2	π	+0.017	+0.006	+0.013	-0.039	-0.037	-0.057	+0.077
h_{O8} = +0.193	σ	-0.054	-0.044	-0.038	+0.056	+0.225	-0.195	-0.368
h_{O9} = +1.379	$(\sigma+\pi)$	-0.037	-0.038	-0.025	+0.017	+0.188	-0.252	-0.291
K = 1.4	π	+0.014	+0.005	+0.013	-0.029	-0.001	-0.093	+0.072
h_{O8} = +0.312	σ	-0.041	-0.034	-0.033	+0.038	+0.170	-0.119	-0.304
h_{O9} = +1.471	$(\sigma+\pi)$	-0.027	-0.029	-0.020	+0.009	+0.169	-0.212	-0.232

$\beta_{CO_8} = 2.0\beta_{CC}$ $\beta_{CO_9} = 0.9\beta_{CC}$

TABLE 6·7 COMPUTED CHARGES IN BENZOIC ACID FOR VARIOUS SIGMA BOND PARAMETERS.

Not all the molecules computed contained heteroatoms, however. Some hydrocarbons were computed too. The results for butadiene are presented in table 6.8.

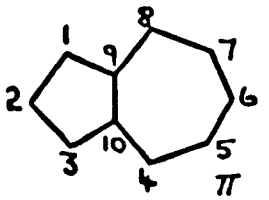


		ATOM	
		1	2
K = 1.0	π	+0.007	-0.007
	σ	-0.088	-0.065
	$(\sigma+\pi)$	-0.081	-0.072
K = 1.2	π	+0.008	-0.008
	σ	-0.076	-0.051
	$(\sigma+\pi)$	-0.068	-0.059
K = 1.4	π	+0.007	-0.007
	σ	-0.060	-0.038
	$(\sigma+\pi)$	-0.053	-0.045
K = 1.6	π	+0.006	-0.006
	σ	-0.043	-0.024
	$(\sigma+\pi)$	-0.037	-0.030

$\beta_{23} = \beta_{12} = \beta_{CC}$

TABLE 6·8 COMPUTED CHARGES IN BUTADIENE FOR VARIOUS SIGMA BOND PARAMETERS.

Since azulene is something of a test case for M. O. calculations, this molecule was also computed. In most M.O. calculations carbon atom 1 bears greatest π charge with carbon atom 5 having the next greatest π charge. The results obtained by I.S.C.C.M. are shown in table 6·9.



		ATOM					
		1	2	4	5	6	9
K = 1·0	π	-0·135	-0·029	+0·121	+0·008	+0·104	-0·031
	σ	+0·034	-0·064	-0·141	-0·041	-0·122	-0·021
	$(\sigma+\pi)$	-0·101	-0·093	-0·020	-0·033	-0·018	-0·052
K = 1·2	π	-0·125	-0·029	+0·112	+0·010	+0·096	-0·030
	σ	+0·023	-0·056	-0·111	-0·031	-0·096	-0·012
	$(\sigma+\pi)$	-0·102	-0·085	+0·001	-0·021	0·000	-0·042
K = 1·4	π	-0·117	-0·031	+0·104	+0·013	+0·089	-0·028
	σ	+0·016	-0·045	-0·084	-0·023	-0·072	-0·005
	$(\sigma+\pi)$	-0·101	-0.076	+0·020	-0·010	+0·017	-0·033
K = 1·6	π	-0·110	-0·033	+0·094	+0·016	+0·018	-0·025
	σ	+0·011	-0·032	-0·055	-0·015	-0·047	-0·002
	$(\sigma+\pi)$	-0·099	-0·065	+0·039	+0·001	+0·034	-0·027

TABLE 6·9 COMPUTED CHARGES IN AZULENE FOR VARIOUS SIGMA BOND PARAMETERS.

The experimentally determined dipole moment for azulene is 0·8D[116].

The calculated dipole moments are presented in table 6·10.

CALCULATION	DIPOLE MOMENTS (Debyes)		
K = 1·0	0·628	5·018	4·390
K = 1·1	0·740	4·690	3·950
K = 1·2	0·263	4·725	4·462
K = 1·3	0·161	4·621	4·460
K = 1·4	0·168	4·526	4·358
K = 1·5	0·074	4·398	4·324
K = 1·6	0·085	4·306	4·221

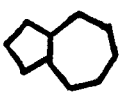


TABLE 6·10 CALCULATED DIPOLE MOMENTS IN AZULENE.

(vi) Discussion and Conclusion.

(1) Pyridine

The main feature to be noted from table 6·2 is the sensitivity of the nitrogen atom to the sigma distribution. h_n increases as the gross sigma charge on the atom decreases, and the gross pi charge consequently increases. However, a given change in sigma charge at the nitrogen atom produced a correspondingly smaller change in pi charge. Atoms 2 and 4 are less sensitive to changes in charge, while for atom 3 the pi charge hardly varies at all. The order of increasing π charge in calculations K = 1·3 and above, is

$$N_1 > C_2 > C_3 > C_4$$

which is similar to the order produced in other calculations on pyridine, though the ordering of charges on atoms 2 and 3 is frequently reversed in the latter. (see table 6·11)

The total dipole moment calculated in a very approximate manner improves throughout the calculations, the sigma electronic dipole moment being reduced relative to that of the pi electrons. Although the electronic energy is not an accurate quantity it is interesting to note that it improves as we go from K = 1·0 ($E = 7·6370\beta$) to K = 1.6 ($E = 8·2281\beta$).

Clearly there is an improvement regarding the computation of pyridine as the magnitude of the sigma electronic charge on the nitrogen atom decreases.

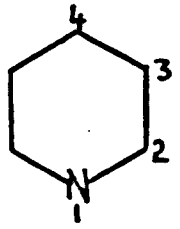
(2) Pyrrole.

In pyrrole (table 6·3) the pi charge flows from the carbon atoms to the nitrogen atom as the sigma charge transfer to the nitrogen through the C-N bonds decreases. A decrease in sigma charge produces a correspondingly smaller increase in pi charge. The general qualitative features of both sigma and pi electron distributions remain the same throughout and these are similar to those reported by other workers (see table 6·3). The dipole moments (table 6·5) improve throughout the calculations although

ATOM	ab initio (95a)			VESCF (109)	SCFPPP (110)	SCF (111)	SCFPPP (112)
	σ	π	σ+π	π	π	π	π
1	-0·216	-0·010	-0·226	-0·096	-0·208	-0·100	-0·234
2	-0·105	-0·005	-0·110	+0·036	+0·095	+0·049	+0·109
3	-0·223	-0·002	-0·225	+0·003	-0·012	-0·010	-0·012
4	-0·227	+0·025	-0·202	+0·016	+0·042	+0·021	+0·039

ATOM	MINDO (113)			I.S.C.C.M. (K=1·3)		
	σ	π	σ+π	σ	π	σ+π
1	-0·220	-0·323	-0·543	-0·172	-0·028	-0·210
2	+0·218	+0·177	+0·395	+0·017	-0·009	+0·008
3	+0·010	-0·091	-0·081	-0·037	+0·015	-0·022
4	+0·029	+0·153	+0·182	-0·043	+0·016	-0·027

TABLE 6·11 ELECTRONIC CHARGES IN PYRIDINE.



none of the computed values differs greatly from the experimental result.

(3) Furan

The furan molecule shows a rather similar behaviour to pyrrole. The gross pi charge on the oxygen atom increases although the corresponding decreases in the gross sigma charge are of a larger magnitude. The computed charge distributions are similar to other reported values (see table 6.12).

ATOM	CNDO (114)			VESCF (106)	SCFPPP (108)	ISCCM (K=1.0)		
	σ	π	σ+π	π	π	σ	π	σ+π
1	-0.609	+0.295	-0.314	+0.205	+0.150	-0.746	+0.407	-0.339
2	+0.262	-0.067	+0.194	-0.046	-0.040	+0.152	-0.116	+0.036
3	+0.004	-0.080	-0.080	-0.056	-0.035	+0.037	-0.086	-0.049

ATOM	ISCCM (K=1.4)		
	σ	π	σ+π
1	-0.401	+0.271	-0.130
2	+0.112	-0.080	+0.032
3	0.000	-0.055	-0.055

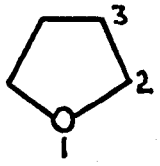


TABLE 6.12 ELECTRONIC CHARGES IN FURAN

(4) Benzoic Acid

Overall the gross total charges do not change appreciably quantitatively or qualitatively. (table 6.7) The sigma charges retain the same qualitative features except for atoms 2 and 3 which assume similar net sigma charges when K = 1.4. The most noticeable change in the pi electron distribution is the loss of pi charge from carbon atom 7 to its neighbouring oxygen atoms. It is gratifying to note that the ortho and para carbon atoms are more negative than the meta one, in keeping with V.B. theory.

(5) Butadiene

In this molecule the pi electron charges (table 6.9) hardly alter

throughout the series. Reducing β_{23} to 0.75β made almost no difference to the charge distribution, either sigma or pi. Results indicate carbon atom 1 to bear a larger pi charge and a larger sigma charge than atom 2 (89). The I.S.C.C.M. result shows the latter result but not the former one.

(6) Azulene

In each computation in the series the gross pi charge on atoms 5 and 7 is less than that on atom 2, in disagreement with a number of other results.

As in the case of butadiene the pi electron charges vary from atom to atom in an almost opposite manner to the sigma charge variation. There is little improvement in the calculated dipole moment (table 6·10) nor is there much change in the electronic energy, $E = 12{\cdot}1207\,\beta$ for $K = 1{\cdot}0$, $E = 12{\cdot}8150\beta$ for $K = 1.6$.

The awkward feature of the results for azulene is that far too high a proportion of the pi charge resides on the atoms in the 5 - membered ring.

(vii) General Observations

The following observations are made

(a) The use of the I.S.C.C.M. seems to give quite reasonable charge distributions for pyrrole, furan and benzoic acid for all sigma parameter sets.

(b) The charge distribution for pyridine becomes closer to that reported by other workers and the calculated dipole moment improves steadily as the sigma charge on the nitrogen atom is reduced in magnitude.

(c) Little improvement is noted in the hydrocarbons studied, no matter which sigma bond parameters are used. The repulsive effect of the sigma electrons on the pi electron distribution in those molecules appears to be too pronounced.

(viii) General considerations and conclusion.

On the whole the results of the I.S.C.C.M. calculations are indeterminate. A possible source of error, i.e. the magnitude of the sigma charge transfers, has been investigated with mixed success.

However, the problems facing I.S.C.C.M. could lie elsewhere.

An iterative scheme of the sort involved in I.S.C.C.M. is based on the assumed symmetry of sigma and pi inductive effects. The idea is that the sigma charge density of an atom affects directly the ionisation potential of the pi electron orbital and vice versa. The interaction of the sigma and pi electrons is expressed through parametric equations of the form

$$h_X = A + Bq_X + Cq_X^2 \qquad (6\cdot2)$$

This is the only sigma - pi interaction considered in I.S.C.C.M. In simple Hückel methods, on the other hand, the h_X "inductive" parameters are chosen on a semi-empirical basis. It is highly likely that the h_X values represent a complex of core - pi electron interactions which include more than simple inductive effects. In I.S.C.C.M., on the other hand, an attempt is being made to set up a fairly rigorous calculation in which the h_X parameters are given a precise theoretical meaning.

The main problem arising from the h_X parametric expressions is that a build up of sigma electrons at a particular atom leads automatically to a lowering of the pi orbital I.P. and therefore of the absolute magnitude of the diagonal matrix element. The result is that the variation of pi electron charges in a molecule is in an opposite direction to the variation of sigma charges. Coulson shows that increasing polarity towards oxygen in C-O bonds in carbonyl molecules decreases the I.P.s of the lone pairs on the oxygen[115]. I.S.C.C.M. exhibits a similar phenomenon in the case of pi electrons

in conjugated molecules. This comes out most strikingly in the case of those molecules which contain pyridine type nitrogen atoms, although other methods do not show this effect. The same sort of thing happens in butadiene. Momicchioli and del Re, for example, using a modified P.P.P. method[89], find that atom 1 carries both a higher sigma and a higher pi charge density on the same atom.

It is the author's opinion that the I.S.C.C.M. overestimates the effects of the sigma charge distribution on the pi orbital I.P.s.

Chapter 7

An S.C.F.P.P.P. ($\sigma + \pi$) method.

(i) Introduction

The changes in π electron distribution as the magnitude of the sigma charges on the atoms is reduced have been noted in chapter 6. In particular this change in sigma charge is pronounced at the nitrogen atom in pyridine and the polarity of the C-N sigma bonds was reduced considerably through the set of calculations. For the K = 1.0 calculation, that is using σ bond parameters based on the completely correlated charge function equation (3·14), the σ charge transfer (towards nitrogen) in the C-N bond in pyridine is about 0.15 electrons. This compares well with a recent ab initio computation of the hypothetical molecule "formaldimine" (figure 7·1) which gives a charge shift of 0·135 electrons in the C-N sigma bond[117].

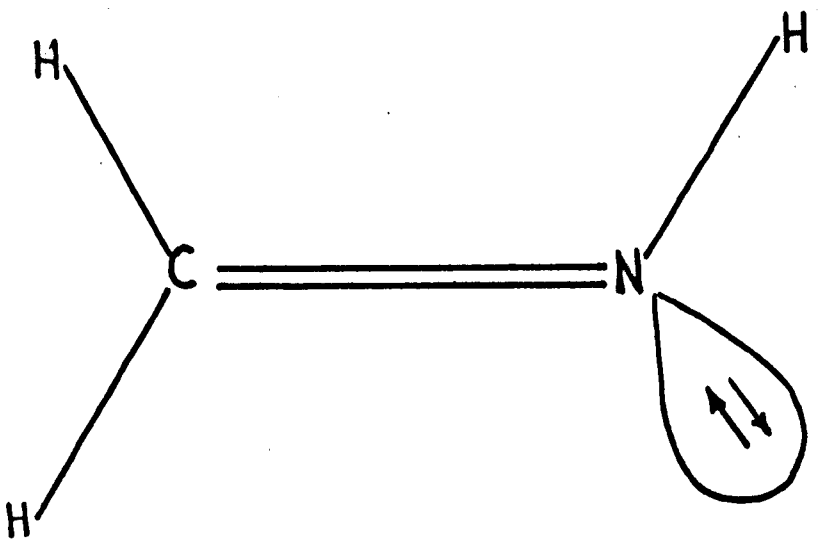


FIGURE 7·1 THE HYPOTHETICAL MOLECULE "FORMALDIMINE".

In view of this result the charge transfer calculated by the sigma method used in this work is not unreasonable. For other reasons, for example the relatively successful computation of sigma charges in saturated molecules and the N.Q.R. results discussed earlier in this thesis the sigma calculation also appears fairly reliable. This leads us to a search for a more adequate combination of the sigma method with a pi electron method. The P.P.P. method[88a,b] is chosen for this purpose.

In this chapter molecules containing heteroatoms are discussed with special consideration for the pyridine molecule.

(ii) The basic approach.

There is a fundamental change in the method of calculation. Formerly the method consisted of a computation of the pi electron distribution followed by a sigma charge calculation using the pi charges so obtained to give a set of sigma charges which are then used to compute the V.S.I.P.s appearing in the diagonal elements of the next cycle of the pi calculations. This iterative process is then continued to convergence of the pi electron energy. In the new approach an initial sigma charge distribution is computed assuming unit pi charges and the resulting sigma charges then serve to provide a constant potential framework for the S.C.F.P.P.P. calculation on the pi electron system. A similar approach has been tried by Momicchioli and del Re[89].

(iii) Preliminary calculations on pyridine.

Calculation 1 Unit pi charges are used for the sigma calculation. Valence state energy data are those of Hinze and Jaffe[20], and V.S.I.P.s and V.S.E.A.s for the pi orbitals are computed from the resulting sigma electron distribution. The one centre repulsion integrals γ_{ii} are obtained from the Pariser-Parr approximation.

$$\gamma_{ii} = I_i - A_i \qquad (7.1)$$

and the two centre repulsion integrals γ_{ij} are computed using the Ruedridge-Hinze approximation[118]

$$\gamma_{ij} = 1/(a \exp(-r_{ij}^2/2) + r_{ij}) \quad (7\cdot2a)$$

where $$a = 2/(\gamma_{ii} + \gamma_{jj}) \quad (7\cdot2b)$$

The V.S.I.P.s, and γ_{ii} and γ_{jj} terms are then held constant throughout the pi electron calculation which is a straightforward S.C.F.P.P.P. one. The results are presented in table 7·1.

ATOM	Net σ charge	Net π charge	
1	-0.286	+0·043	β_{CN} = -2·47eV
2	+0·001	-0·046	β_{CC} = -2·39eV
3	-0·038	+0·023	E = -54·6804eV
4	-0·047	+0·004	I.P.= 10·7270eV

TABLE 7·1 CALCULATION 1 OF PYRIDINE - RESULTS.

(Numbering system as in Chapter 6)

Calculation 2 Unit pi charges are again used for the sigma calculation. The V.S.I.P.s and one - and two - centre integrals are all dependent on the total ($\sigma + \pi$) charges on each cycle. The results are presented in table 7·2.

ATOM	Net σ charge	Net π charge	
1	-0·286	+0·013	β_{CN} = -2·47eV
2	+0·001	-0·016	β_{CC} = -2·39eV
3	-0·038	+0·006	E = -54·6580eV
4	-0·047	+0·002	I.P.= 10·7745eV

TABLE 7·2 CALCULATION 2 OF PYRIDINE - RESULTS.

Calculation 3 As in calculation 1 and 2, unit pi charges are used for the sigma calculation. Neutral atom V.S.I.P.s and V.S.E.A.s from Hinze's and Jaffe's tables are used to compute the one-centre and two-centre repulsion integrals which are then held constant through the pi calculation. The V.S.I.P.s used in the diagonal elements are obtained from the sigma charges. The results are presented in table 7·3.

ATOM	Net σ charge	Net π charges	
1	-0·286	+0·107	β_{CN} = -2·47eV
2	+0·001	-0·083	β_{CC} = -2·39eV
3	-0·038	+0·006	E = -53·8162eV
4	-0·047	+0·047	I.P.= 10·4937eV

TABLE 7·3 CALCULATION 3 OF PYRIDINE - RESULTS.

(iv) Appraisal of calculations 1, 2 and 3.

As in the case of the I.S.C.C.M.. ($\sigma + \pi$) calculations discussed earlier, the π charges are very low compared to those given by other methods. The reason is, once again, that the diagonal elements for the nitrogen atom are too low and those for the carbons too high. In calculation 3, for example, on the first cycle of the π calculation immediately after the σ calculation the diagonal elements are

N : -4·46879 C_1 : -5·6404 C_2 : -5·17897

C_3: -4·59219 (all in eV)

This problem in turn stems from the low V.S.I.P. of the nitrogen atom which is 10·6388eV whereas the adjacent carbon has a V.S.I.P. of 11·1690eV. Consequently, the nitrogen is certain to lose π charge to the adjacent carbons. It may be the case that the Hinze-Jaffe formulas for valence state energy data do give V.S.I.P.s for nitrogen which are lower than is desirable in these calculations.(146) An alternative scheme suggests itself. This is based on the techniques used in the V.E.S.C.F. method of Brown and Heffernan. In this method the V.S.I.P.s and the diagonal

elements are rendered charge dependent by means of quadratic functions of the effective nuclear charge. These expressions are transformed into explicit functions of the σ and π charges on the atoms.

(v) V.S.I.P. expressions derived from quadratic functions of the nuclear charge.

In an early paper[119] Brown and Heffernan give the following expression for the V.S.I.P. of trigonally hybridised carbon.

$$I_C = 3{\cdot}490\ Z_C^2 - 9{\cdot}767 Z_C + 4{\cdot}048 \qquad (7{\cdot}3)$$
$$(\text{tr tr tr } \pi \longrightarrow \text{tr tr tr})$$

When deriving this expression Z_C, the effective nuclear charge, is the mean of the Slater values for C and C^+. This averaging makes allowance for the change in Z_C accompanying the actual ionisation because in the V.E.S.C.F. method in which the equation is used I_C is required for a constant Z_C. Emsley gives the following expression for the same process[120].

$$I_C = 3{\cdot}4Z_C^2 - 9{\cdot}096\ Z_C + 2{\cdot}5006 \qquad (7{\cdot}4)$$

For C (tr tr tr π), by Slater's rules

$$Z_C = 6 - 1{\cdot}35 - 0{\cdot}35\ (\sigma_c + P_{cc}) \qquad (7{\cdot}5)$$

where σ_c and P_{cc} are the gross sigma and pi charges on the atom respectively, i.e.

$$Z_C = 4{\cdot}65 - 0{\cdot}35\ (\sigma_c + P_{cc}) \qquad (7{\cdot}6)$$

and

$$Z_C^+ = 6 - 1{\cdot}35 - 0{\cdot}35\ (\sigma_c + P_{cc}) + 0{\cdot}35 \qquad (7{\cdot}7)$$

i.e.

$$Z_C^+ = 5 - 0{\cdot}35\ (\sigma_c + P_{cc}) \qquad (7{\cdot}8)$$

since the nuclear charge is increased by the opposite of the amount of shielding due to one electron in the positive ion. The Z_C to be used in the calculation is then the average of equations (7·6) and (7·8), i.e.

$$Z_C = 4{\cdot}825 - 0{\cdot}35\ (\sigma_c + P_{cc}) \qquad (7{\cdot}9)$$

If we put $P_{cc} = 1$ the effective nuclear charge depends on the sigma electronic charge through the relation.

$$Z_C = 4{\cdot}475 - 0{\cdot}35\,\sigma_C \qquad (7{\cdot}10)$$

Inserting (7·10) in (7·4) leads to the following equation for the carbon pi orbital V.S.I.P.

$$I_C = 29{\cdot}884 - 7{\cdot}469\,\sigma_c + 0{\cdot}417\,\sigma_c^2 \qquad (7{\cdot}11)$$

It is now straightforward to transform equation (7·11) which is dependent on the total sigma charge density at the atom to the corresponding function of the net sigma electron charge because $\sigma_C = 3 - Q_c$ where Q_c is the net sigma charge on the atom.

The resulting expression is

$$I_C = 11{\cdot}230 + 4{\cdot}967\,Q_c + 0{\cdot}417\,Q_c^2 \qquad (7{\cdot}12)$$

For comparison the same procedure was carried out on other expressions relating V.S.I.P. to effective nuclear charge. The author also generated another similar expression by plotting the pi orbital V.S.I.P.s of the isoelectronic (to trigonally hybridised carbon) series B^-, C, N^+, O^{2+} and F^{3+} against Z. The data were obtained from a paper by Edlen[121] and the resulting quadratic is included in table 7·4 alongside the others.

	$I_c = AZ_c^2 + BZ_c + C$			Ref.	$I_c = D + EQ_c + FQ_c^2$		
	A	B	C		D	E	F
I	+0·3605	+9·092	-21·818	(103)	+11·538	+4·003	+0·084
II	+3·490	-9·767	+4·048	(119)	+11·535	+4·948	+0·428
III	+3·4	-9·096	+2·501	(120)	+11·230	+4·967	+0·417
IV	+3·678	-11·165	+6·350	*	+11·254	+4·909	+0·451
V				(20)	+11·163	+11·196	+1·319

* Author's result

TABLE 7·4 QUADRATIC FUNCTIONS OF V.S.I.P. OF TRIGONALLY HYBRIDISED CARBON.

The interesting point about the expressions in table 7·4 is that of the charge dependent expressions the magnitude of coefficient E in Hinze's and co-workers quadratic (V) is at least double that of any of the others.

It was felt that if the alternative functional expressions for the V.S.I.P. of the pi orbital of the pyridine type nitrogen atom also led to a smaller linear coefficient it could have important consequences for the pi electron distribution in pyridine. Hence the trigonally hybridised nitrogen atom was treated in the same sort of way.

The effective nuclear charge for N (tr tr $tr^2\pi$) is related to the gross sigma charge on the nitrogen atom by

$$Z_N = 5\cdot475 - 0\cdot35\ \sigma_N \qquad (7\cdot13)$$

In this treatment the functional relation - expressing the V.S.I.P. of the pi orbital on the nitrogen atom in terms of Z_N - chosen is that due to Ensley[120].

$$I_N = 3\cdot3675\ Z_N^2 - 10\cdot8535\ Z_N + 2\cdot7304 \qquad (7\cdot14)$$

I_N as a function of the gross sigma charge on the atom is obtained by substituting equation (7·13) in (7·14),

$$I_N = 44\cdot252 - 9\cdot109\ \sigma_N + 0\cdot413\ \sigma_N^2 \qquad (7\cdot15)$$

Since the gross and net sigma charges on nitrogen are related by

$$\sigma_N = 4 - Q_N \qquad (7\cdot16)$$

where Q_N is the net sigma charge, the final charge - dependent expression is readily obtained

$$I_N = 14\cdot424 + 5\cdot805\ Q_N + 0\cdot413\ Q_N^2 \qquad (7\cdot17)$$

The Hinze function is

$$I_N = 14\cdot144 + 12\cdot701\ Q_N + 1\cdot894\ Q_N^2 \qquad (7\cdot18)$$

Again the linear coefficient in the equation derived from the Z_N function is smaller than the corresponding one in Hinze's expression.

Using Edlen's data for the V.S.I.P.s of the isoelectronic series C-, N, O^+ and F^{2+}, analysis produced the quadratic expression

$$I_N = 3{\cdot}512\ Z_N^2 - 11{\cdot}997\ Z_N + 4{\cdot}806 \qquad (7{\cdot}19)$$

and eventually one arrives at the charge dependent function

$$I_N = 14{\cdot}214 + 5{\cdot}825\ Q_N + 0{\cdot}430\ Q_N^2 \qquad (7{\cdot}20)$$

The three functions are summarised in table 7·5.

	$I_N = AZ_N^2 + BZ_N + C$			Ref	$I_N = D + EQ_N + FQ_N^2$		
	A	B	C		D	E	F
I	+3·3675	-10·8535	+2·7304	(120)	+14·424	+5·805	+0·413
II	+3·512	-11·997	+ +4·806	*	+14·214	+5·825	+0·430
III				(20)	+14·114	+12·701	+1·894

* Authors result.

TABLE 7·5 QUADRATIC FUNCTIONS OF V.S.I.P. OF TRIGONALLY HYBRIDISED NITROGEN.

The consequences of these findings are illustrated by a simple consideration. The sigma electron calculation on pyridine gives $Q_N = -0{\cdot}29$, $Q_C = 0{\cdot}00$. Inserting these values into equations V of table 7·4 and III of table 7·5 respectively, the Hinze expression gives

$$I_C = 11{\cdot}163\text{eV}$$

$$I_N = 10{\cdot}469\text{eV}$$

Thus the V.S.I.P. of the nitrogen is lower than that of the carbon leading almost inevitably to pi charge transfer from nitrogen to carbon. Inserting the above net charges into equations IV of table 7·4 and II of table 7·5 respectively, on the other hand, gives

$$I_C = 11{\cdot}254\text{eV}$$

$$I_N = 12{\cdot}561\text{eV}$$

The direction of pi charge transfer is now likely to be from carbon to nitrogen because the magnitude of the diagonal element for nitrogen will be increased relative to that for carbon.

The one-centre repulsion integrals for nitrogen (tr tr $tr^2\pi$) and carbon (tr tr tr π) are calculated in a different manner, too. A variant of Paolini's formula[122]

$$\gamma_{ii} = 3{\cdot}294\, Z_i \qquad (7{\cdot}21)$$

is used.

Equation (7·21) applied to nitrogen and carbon is rendered charge dependent in a manner similar to transformations described earlier. The resulting equations for γ_{cc} and γ_{NN} are

$$\gamma_{cc} = 11{\cdot}282 + 1{\cdot}153\, Q_C \qquad (7{\cdot}22)$$

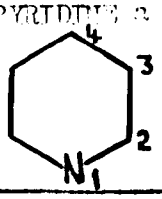
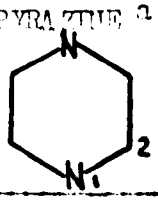
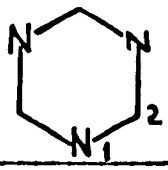
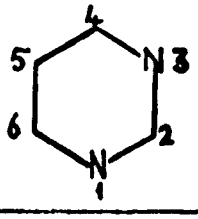
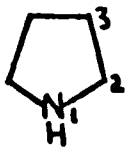
$$\gamma_{NN} = 12{\cdot}846 + 1{\cdot}153\, Q_N \qquad (7{\cdot}23)$$

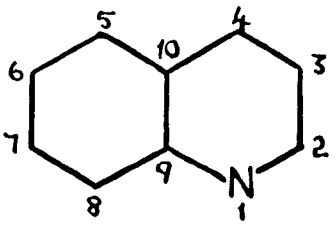
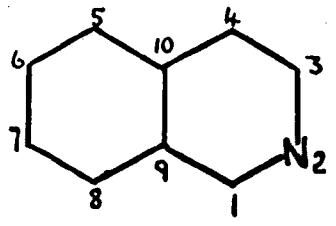
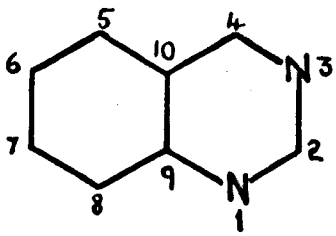
where the Q's signify net electronic charges on the atoms. The one-centre repulsion integrals for other atoms occurring in the molecules studied are computed using the Pariser-Parr formula.

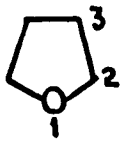
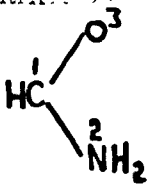
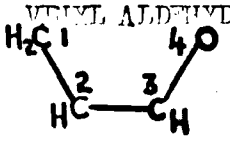
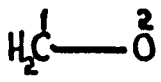
The results of computations of several molecules are presented in the next section. The computer program used in the calculations and its area of applicability are described in appendix IV.

(vi) Results of Calculations

The electronic charge distributions in several molecules have been computed using the P.P.P. (σ+ π) method described in the last chapter. The computed charges are presented in table 7·6.

CALCULATION*	MOLECULE	NET σ-CHARGE	NET π CHARGE	CALC. I.P. (eV)
I	PYRIDINE a 	1. -0·286 2. +0·001 3. -0·038	1. -0·042 2. +0·009 3. +0·007	10·6647
II	PYRAZINE a 	1. -0·268 2. +0·025	1. -0·034 2. +0·017	10·9053
III	S-TRIAZINE a 	1. -0·226 2. +0·086	1. -0·033 2. +0·033	11·5421
IV	PYRIMIDINE a 	1. -0·256 2. +0·068 4. +0·016 5. -0·014	1. -0·038 2. +0·019 4. +0·022 5. +0·015	11·0091
V	PYRROLE a 	1. -0·197 2. +0·044 3. +0·014	1. +0·282 2. -0·080 3. -0·062	10·2850

CALCULATION*	MOLECULE		NET σ CHARGE		NET π CHARGE	CALC. I.P. (eV)
VI	QUINOLINE [a]	1.	−0·278	1.	−0·067	
		2.	+0·004	2.	+0·022	
		3.	−0·034	3.	+0·007	
		4.	−0·039	4.	+0·016	
		5.	−0·045	5.	+0·002	9·88517
		6.	−0·052	6.	+0·005	
		7.	−0·050	7.	+0·007	
		8.	−0·033	8.	+0·006	
		9.	+0·020	9.	+0·002	
		10.	−0·017	10.	0·000	
VII	ISOQUINOLINE [a]	1.	+0·008	1.	+0·020	
		2.	−0·282	2.	−0·062	
		3.	+0·004	3.	+0·011	
		4.	−0·030	4.	+0·009	
		5.	−0·048	5.	+0·002	9·85139
		6.	−0·055	6.	+0·006	
		7.	−0·054	7.	+0·005	
		8.	−0·045	8.	+0·001	
		9.	−0·016	9.	0·000	
		10.	−0·025	10.	+0·004	
VIII	QUINAZOLINE [a]	1.	−0·249	1.	−0·060	
		2.	+0·071	2.	+0·032	
		3.	−0·253	3.	−0·061	
		4.	+0·023	4.	+0·039	
		5.	−0·037	5.	+0·006	10·1201
		6.	−0·049	6.	+0·009	
		7.	−0·047	7.	+0·012	
		8.	−0·028	8.	+0·008	
		9.	+0·034	9.	+0·011	
		10.	+0·005	10.	+0·004	

CALCULATION*	MOLECULE	NET σ CHARGES	NET π CHARGES	CALC. I.P. (eV)
IX	FURAN[b] 	1. -0·153 2. +0·173 3. +0·031	1. +0·157 2. -0·061 3. -0·018	10·8187
X	FORMAMIDE[c] 	1. +0·130 2. -0·281 3. -0·309	1. -0·073 2. -0·156 3. -0·083	9·68500
XI	VINYL ALDEHYDE[c] 	1. -0·173 2. -0·114 3. -0·280 4. -0·334	1. +0·031 2. +0·010 3. -0·054 4. +0·014	10·3600
XII	FORMALDEHYDE[c] 	1. +0·069 2. -0·337	1. 0·000 2. 0·000	12·4969

* Geometries are from Sutton[123]. If the experimentally determined geometry was not available, the geometry was constructed using standard bond lengths, also quoted in Sutton.

a. $\beta_{CN} = \beta_{CC} = -2{\cdot}39$ eV

b. $\beta_{CO} = -2{\cdot}50$ eV $\quad \beta_{CC} = -2{\cdot}39$ eV

c. $\beta_{CN} = \beta_{CC} = -2{\cdot}39$ eV $\quad \beta_{CO} = -2{\cdot}69$ eV

TABLE 7·6 ELECTRONIC CHARGE DISTRIBUTIONS CALCULATED BY THE P.P.P. ($\sigma + \pi$) METHOD.

Molecular I.P.s (vertical) were calculated using Koopman's theorem[124]. The values are reported in table 7·7, and a plot of calculated versus experimental results is shown in figure 7·2. The difference between the calculated and experimental results for the first nine molecules is fairly constant.

MOLECULE	I.P.(CALC)eV	I.P.(EXP'T)eV	ΔC - E
Pyridine (1)	10·66	9·52 a	1·14
Pyrazine (2)	10·91	9·62 b	1·29
Pyrimidine (3)	11·01	9·69 b	1·32
S-Triazine (4)	11·54	10·07 c	1·47
Quinoline (5)	9·89	8·62 d	1·27
Isoquinoline (6)	9·85	8·55 d	1·30
Quinoxaline (7)	10·36	9.02 d	1·34
Quinazoline (8)	10·12	9·02 e	1·10
Pyrrole	10·29	8·59 b	1·70
Furan	10·82	8·77 f	2·05
Formamide	9·69	10·84 g	-1·15
Vinyl Aldehyde	10·36	10·20 h	0·15
Formaldehyde	12·50	10·87 f	1·63

a. Mean of photoelectron[125] and electron impact[126] values.

b. Mean of P.E.[127] and E.I.[126] results.

c. E.I.[126] results.

d. Photoionisation value[128].

e. P.E. result[129].

f. P.E. result[127].

g. P.E. result[130].

h. Mean of P.E.[131] and E.I.[132].

TABLE 7·7 MOLECULAR IONISATION POTENTIALS.

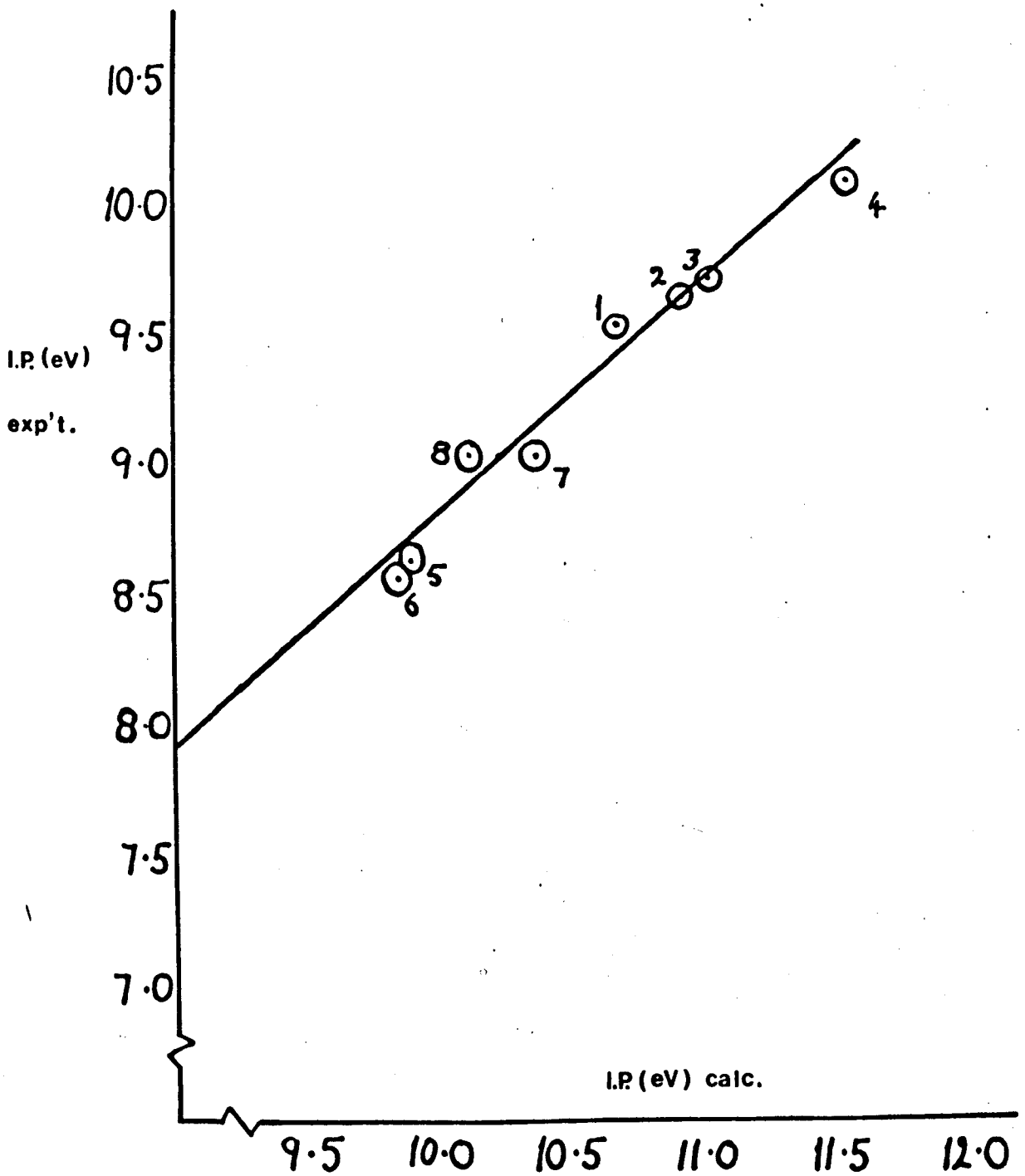


FIGURE 7.2 PLOT OF CALCULATED I.P.S AGAINST EXPERIMENTAL I.P.S.

The equation of the line in figure 7·2 is

$$I.P._{Exp} = 0.89\ I.P._{CALC} - 0.12 \qquad (7.24)$$

Applying this equation to the calculated I.P.s for molecules (1) to (8) one obtains the results shown in table 7·8.

MOLECULE	I.P.(CALC)eV	I.P. (EXP) eV
1.	9·37	9·52
2.	9·59	9·62
3.	9·68	9·69
4.	10·15	10·07
5.	8.68	8.62
6.	8·65	8·55
7.	9·10	9·02
8.	8·89	9·02

TABLE 7·8 MODIFIED CALCULATED I.P.s.

The calculated molecular I.P.s for the other molecules - excluding pyrrole - are in much poorer agreement with experiment.

(vii) Discussion and conclusion.

1. Pyridine

The π electron charge distribution in pyridine is now similar to the distributions obtained by other methods. It resembles the ab initio results rather more than the results of other methods. The π electron charges on the carbon atoms are all low. (see figures 7.3a and 7.3b)

2. Pyrazine, S-Triazine, Pyrimidine.

Again, the present charge distributions resemble those obtained in other methods. A comparison of results is made in table 7·9

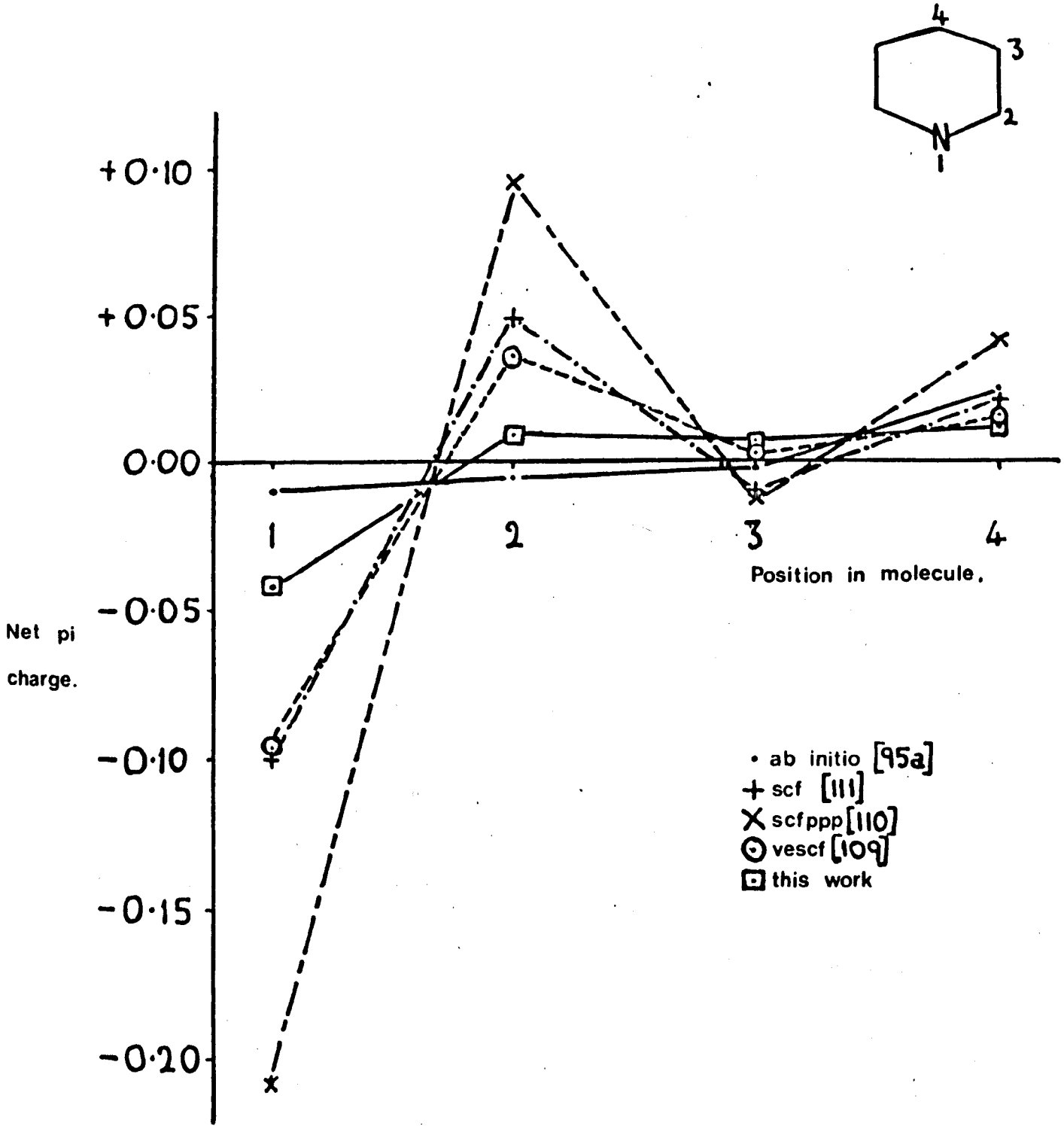


FIGURE 7.3a. NET PI CHARGES IN PYRIDINE.

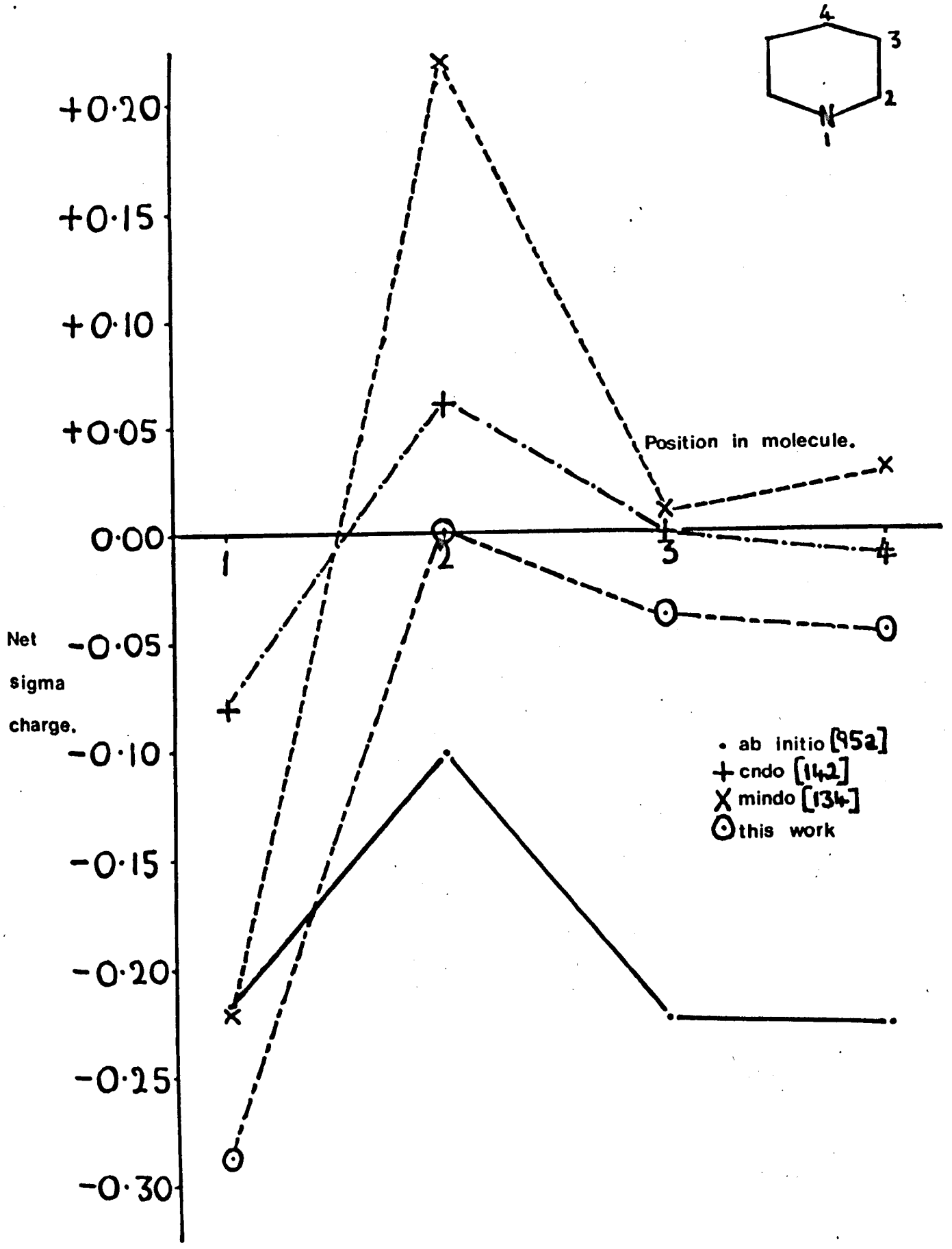
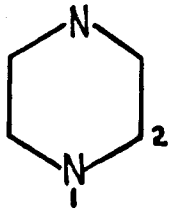


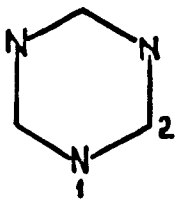
FIGURE 7.3b. NET SIGMA CHARGES IN PYRIDINE.

PYRAZINE



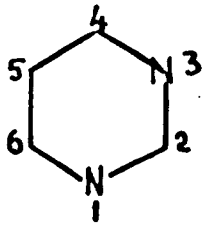
ATOM	THIS WORK	VESCF[109]	SCF PPP[110]
1.	-0·034	-0·080	-0·171
2.	+0·017	+0·040	+0·085

S-TRIAZINE



ATOM	THIS WORK	SCF[111]	SCG PPP[110]
1.	-0·033	-0·116	-0·231
2.	+0·033	+0·116	+0·231

PYRIMIDINE



ATOM	THIS WORK	VESCF[103]	SCF PPP[110]
1.	-0·038	-0·027	-0·220
2.	+0·019	+0·010	+0·188
4.	+0·022	+0·020	+0·138
5.	+0·015	+0·004	-0·024

TABLE 7·9 NET PI ELECTRON CHARGES IN PYRAZINE, S-TRIAZINE AND PYRIMIDINE.

The pi electron distributions in these molecules calculated in this work are qualitatively similar to the distributions calculated by other methods. A marked feature of the present results is the generally smaller magnitude of the pi charges on the nitrogen and on the carbon atoms. The VESCF results are of a similar order of magnitude but the SCFPPP results show considerably larger values.

In table 7·10 the sigma electron distributions in pyrimidine are compared.

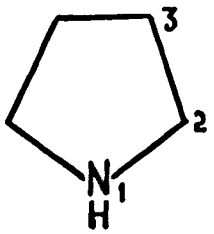
ATOM	THIS WORK	SCF PPP[133]	MINDO[134]
1.	-0·256	-0·135	-0·167
2.	+0·068	+0·084	+0·269
4.	+0·016	+0·028	+0·150
5.	-0·014	-0·018	-0·003

TABLE 7·10 NET SIGMA ELECTRON CHARGES IN PYRIMIDINE.

In the case of the sigma electron distribution the present work produced a larger charge on the nitrogen atom than did the other two methods quoted. The qualitative features of all three sets of results is similar.

3. Pyrrole.

Table 7·11 shows the net charges in pyrrole calculated in the present work compared with results obtained by other methods.



ATOM	THIS WORK		VESCF[106]	SCF PPP[108]
	σ	π	π	π
1.	-0·197	+0·282	+0·281	+0·225
2.	+0·044	-0·080	-0·070	-0·061
3.	+0·014	-0·062	-0·071	-0·052

ATOM	ab initio[107]		CNDO/2[104]	
	σ	π	σ	π
1.	-0·749	+0·341	-0·437	+0·319
2.	-0·030	-0·075	+0·055	-0·095
3.	-0·160	-0·096	+0·137	-0·080

TABLE 7·11 NET ELECTRONIC CHARGES IN PYRROLE.

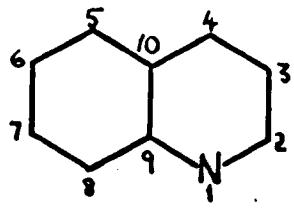
The charges in pyrrole computed in this work show a deficit of pi charge on the nitrogen atom, in common with other results. However, the net sigma charge on this atom is small compared to the ab initio and CNDO/2 results. Unfortunately there is not much agreement among the various methods about the relative order of the pi charges on atoms 2 and 3.

4. Quinoline, Isoquinoline and Quinazoline.

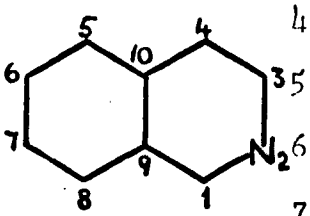
The calculated pi electronic charges in these molecules are presented

in table 7·12.

QUINOLINE ATOM	THIS WORK	SCF PPP[110]	VESCF[109]	SCF[136]
1	-0·067	-0·217	-0·096	-0·239
2	+0·022	+0·116	+0·044	+0·126
3	+0·007	-0·015	-0·002	-0·024
4	+0·016	+0·052	+0·019	+0·060
5	+0·002	+0·003	-0·001	-0·004
6	+0·005	-0·003	0·000	-0·011
7	+0·007	+0·011	-0·004	+0·016
8	+0·006	-0°001	-0·003	-0·015
9	+0·002		+0·024	+0°077
10	0·000		-0·001	+0·014



ISOQUINOLINE ATOM	THIS WORK	SCF PPP[110]	VESCF[109]	SCF[137]
1	+0·020	+0·115	+0·044	+0·146
2	-0·062	-0·209	-0·096	-0·247
3	+0·011	+0·076	+0·029	+0·092
4	+0·009	-0·015	+0·002	-0·019
5	+0·002	-0·003	+0·001	-0·001
6	+0·006	+0·013	+0·005	+0·012
7	+0·005	-0·002	+0·002	0·000
8	+0·004	+0°011	+0·004	+0·002
9	0·000		+0.001	-0.009
10	+0·004		+0.009	+0.024



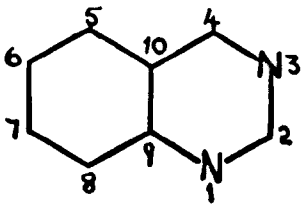
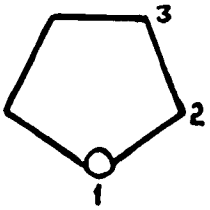
QUINAZOLINE	ATOM	THIS WORK	SCF PPP[110]	VESCF[103]
	1	-0·060	-0·223	-0·029
	2	+0·032	+0·159	+0·073
	3	-0·061	-0·206	-0·097
	4	+0·039	+0·170	+0·064
	5	+0·006	+0·027	+0·006
	6	+0·009	-0·003	+0·003
	7	+0·012	+0·031	+0·009
	8	+0·008	-0·016	+0·004
	9	+0·011	+0·066	+0·035
	10	+0·004	-0·005	+0·002

TABLE 7·12 NET PI ELECTRON CHARGES IN QUINOLINE, ISOQUINOLINE, QUINAZOLINE.

The present results show a higher pi electronic charge on the nitrogen atom than on the other atoms. It is difficult to make any clear cut judgement regarding the pi charges in the rest of the molecule. All methods tend to suggest that the pi charges are near unity on the other atoms.

5. Furan

The calculated electronic charges in furan are presented for comparison in table 7·13. The net sigma charges calculated in the present work agree qualitatively with those of the CNDO calculation, although the charge on the oxygen is much smaller in the former than in the latter. All the calculations produce a net positive pi charge on the oxygen of a similar order of magnitude. The relative order of pi electron charge on atoms 2 and 3 differs from calculation to calculation.



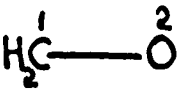
ATOM	THIS WORK σ	THIS WORK π	SCHAAD (108) π
1	−0·153	+0·157	+0·150
2	+0·173	−0·061	−0·040
3	+0·031	−0·018	−0·035

ATOM	CNDO (114) σ	CNDO (114) π	VESCF (106) π	VESCF (103) π
1	−0·609	+0·295	+0·205	+0·206
2	+0·262	−0·067	−0·046	−0·054
3	+0·004	−0·080	−0·056	−0·049

TABLE 7·13 NET ELECTRONIC CHARGES IN FURAN.

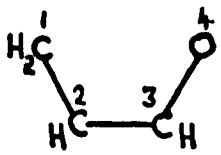
6. Formaldehyde, vinyl aldehyde, formamide.

A comparison of computed electronic charges in these molecules is presented in table 7·14.

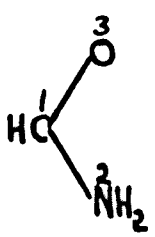


ATOM	THIS WORK σ	THIS WORK π	THIS WORK (σ + π)	CNDO(114) (σ + π)	VESCF(103) π
1	+0·069	0·000	+0·069	+0·211	+0·183
2	−0·337	0·000	−0·337	−0·188	−0·183

ATOM	SCF(113) (σ + π)	INDO(113) (σ + π)
1	+0·177	+0·328
2	−0·230	−0·238



ATOM	THIS WORK σ	THIS WORK π	THIS WORK (σ + π)	CNDO(114) (σ + π)
1	−0·172	+0·031	−0·001	−0·001
2	−0·114	+0·010	−0·134	−0·039
3	−0·280	−0·054	−0·334	+0·235
4	−0·334	+0·014	−0·320	−0·228



ATOM	THIS WORK σ	THIS WORK π	THIS WORK (σ + π)	CNDO(114) (σ + π)
1	+0·130	−0·073	+0·057	+0·356
2	−0·281	+0·156	−0·125	−0·237
3	−0·309	−0·083	−0·392	−0·336

TABLE 7·14 NET ELECTRONIC CHARGES IN FORMALDEHYDE, VINYL ALDEHYDE AND FORMAMIDE.

The present results for formaldehyde show that in considering total net charges all the computations produce a net positive carbon and a net negative oxygen. An unsatisfactory feature of the present work is that the two atoms both have a pi orbital occupancy of one electron. This is surprising in view of the fact that there is a large sigma charge on the oxygen and this would have been expected to lead to an increased pi orbital ionisation potential, and the electronegativity of that atom.

In the case of the other two molecules, the electron distribution in vinyl aldehyde as calculated in the present work bears little similarity to the CNDO result, but the two sets of results for formamide show qualitative agreement.

7. General conclusions.

Overall, the electronic charges calculated using the PPP ($\sigma + \pi$) method are an improvement on ISCCM in the sense that the pi electron distributions compare favourably with other results, at least for the first seven molecules computed. The linking of a separate calculation of the sigma electron distribution with a pi-electron scheme such as the PPP method has an inherent difficulty. The problem is that the W_μ terms, and to a lesser extent the $\gamma_{\mu\mu}$ terms, in the diagonal elements of the PPP Hamiltonian, are semi-empirical parameters. To calculate the W_μ terms on the basis of the valence state scheme used in this work is to identify them, quite specifically, as the VSIP's of the pi electron orbitals on the atoms within the framework of a polarised sigma electron system. In other words in the approach taken in this work the W_μ terms are not semi-empirical parameters.

It is commonly assumed that the introduction of semi-empirical parameters compensates for the simplifications such as the Z.D.O. approximation (e.g. 94). As Freed has pointed out the PPP method is technically an approximation to Hartree-Fock theory, yet its results are sometimes better than those of the full theory when compared with experiment (185). The conclusion Freed draws is that the PPP method is more than an approximation to Hartree-Fock theory. The danger, therefore, is that in removing the semi-empirical basis of the W_μ terms these advantages are lost.

On the other hand it was felt by the author that some attempt should be made to introduce the underlying sigma electron structure particularly as in the cases of molecules like pyridine and pyrrole, when it is probably considerably polarised. In order to keep the method simple these effects were introduced solely through the W_μ and $\gamma_{\mu\mu}$ terms.

Initially when this work was first started there was a much greater need for simplified M.O. calculations than there is now. Computers were not as fast or as efficient as they are now and full SCF calculations on even medium sized molecules of interest to the chemist or biochemist were fairly rare. The Huckel method was in wide use at that time and the present work was directed towards achieving a method as versatile and easy to apply as the former, yet which gave a more complete analysis of the molecular electronic structure. As we have seen this was not possible using the HMO scheme in ISCCM and it was necessary to try a more sophisticated pi electron method in conjunction with the sigma method.

Using the PPP ($\sigma + \pi$) method electronic charge distributions for sigma and pi electrons have been computed which do agree with other more sophisticated calculations in a number of molecules. Given the relatively simple nature of the scheme this is regarded as a success.

APPENDIX I. Derivation of bond charge functions Q_K from Parks and Parr's formulas.

Equation 86 of Parks and Parr's paper "Theory of separated electron pairs" is as follows

$$Q_K = -\sqrt{2}\, H_{12}^K \left(H_{22}^K - H_{11}^K\right)^{-1} \qquad (I.1)$$

where the H's are matrix elements involving bond K, and Q_K is a "polarity parameter" which may be regarded as in ionicity.

According to equation 64 of the paper

$$\left(H_{22}^K - H_{11}^K\right) = -2\beta + \tfrac{1}{4}\left(1-S^2\right)^{-\frac{1}{2}}\left(\gamma_{aa} + \gamma_{bb} - 2\gamma_{ab}\right) \qquad (I.2)$$

and

$$H_{12}^K = \left[2(1-S^2)\right]^{-\frac{1}{2}}\left[(\alpha_a - \alpha_b) + \tfrac{1}{2}(\gamma_{aa} - \gamma_{bb})\right] \qquad (I.3)$$

substitution of equations (I.2) and I.3) in I.1) leads to

$$Q_K = \frac{(1/(1-S^2)^{\frac{1}{2}})(\alpha_a - \alpha_b) - (1/2(1-S^2)^{\frac{1}{2}})(\gamma_{aa} - \gamma_{bb})}{-2\beta + (1/4(1-S^2)^{\frac{1}{2}})(\gamma_{aa} + \gamma_{bb} - 2\gamma_{ab})} \qquad (I.4)$$

Equation (I.4) is the starting point for the amlysis of the bond charge functions in Chapter 3.

APPENDIX II. Definitions of atomic charges in molecules.

Politzer has shown that in the case of diborane two different sets of atomic charges can be obtained from two different ways of defining atomic charges.(138)

Both interpretations cannot be correct but how can one decide which one has a physical meaning?

Mulliken suggested that in L.C.A.O.M.O. theory the charge on an atom A, bearing A.O.'s M and where

$$\Psi_k = \sum_r c_{kr}\psi_r \qquad \text{(II.1)}$$

are the M.O.'s, could be defined as

$$q_A = \sum_k N_k\left(\sum_{\substack{M \\ \text{on} \\ A}} c_{Mk}^2 + \sum_S c_{Mk}c_{Sk}S_{MS}\right) \qquad \text{(II.2)}$$

In the above the C's are coefficients, the ψ's are A.O.s, S is an overlap integral and N_k is the number of electrons in the k^{th} M.O. Politzer has criticised this definition on the grounds that the various pairs of atoms share equally the overlap charge between them, and that there is a small probability of a particular M.O. contributing a negative charge to an atom through the cross terms(138).

A second approach to atomic charges is to orthogonalise the basis functions first using, say, Löwdin's method(139)

$$\{\phi'\} = \{\phi S^{-1/2}\} \qquad \text{(II.3)}$$

where the braces denote matrices. This results in M.O.'s

$$\Psi_k = \sum_a t_{ka} \phi_a \qquad \text{(II.4)}$$

where the ϕ_a are orthogonalised A.O.'s mainly centred on atoms a. The electronic charge on atom A is given by

$$q_A = \sum_k N_k \left(\sum_{\substack{m \\ \text{on} \\ A}} t^2_{mk} \right) \qquad \text{(II.5)}$$

Cross terms have been removed, but now the atomic orbitals ϕ_a cannot be regarded as being associated with atom A because the transformation (II.3) mixes any A.O. with neighbouring A.O.'s.

The dilemma is highlighted by the following example quoted in Politzer's and Mulliken's paper[140]. In the case of the HF molecule two wave functions of very similar quality in terms of basis size and composition and in terms of calculated total energies, a Mulliken population analysis gives different results. One wave function gives +0·23 (H), -0·23(F); the other gives +0.48(H), -0·48(F).

Politzer argues that the problem can only be resolved in terms of the molecular charge distribution and proposes another method for computing atomic charges[141]. In this the total space belonging to the molecules is divided into atomic regions (c.f. Daudel[28]). The electronic density distribution $\rho(\vec{r})$ is then integrated over the region of space belonging to the atom.

$$q_A = \int_A \rho(\vec{r})\, d\vec{r} \qquad \text{(II.6)}$$

Application of this method to the two wave functions for the HF molecule gave nearly identical results. The first wave function gave charges, in

electrons, of +0·27(H), -0·27(F) and the second gave the charges +0·26(H), -0·26(F).

Against these important findings we have to weigh the fact that the method discussed in this thesis is a very approximate one. There is the further consideration that the integrals appearing in the sigma theory are evaluated spectroscopically so that the atomic orbitals on the atoms in the molecule do not appear explicitly in the analysis.

It is assumed that the localised M.O.'s which are the basis of the chemical bonds in the molecule contain two electrons. Hence we write, for example, in the case of a localised M.O., Ψ, representing the bond formed by atoms A and B

$$n_A + n_B = 2 \qquad \text{(II.7)}$$

where n_A is the electronic charge density in the A.O. on A taking part in bond formation with an A.O. on atom B with electronic charge density n_B.

If the underlying basis is orthogonal then

$$n_A = 2c_A^2$$
$$n_B = 2c_B^2 \qquad \text{(II.8)}$$

where C_A is the coefficient of the A.O. on A, and C_B the coefficient of the A.O. on B, in the M.O. Ψ. In the case of a non-orthogonal basis

$$n_A = 2\bar{c}_A^2 + 2\bar{c}_A\bar{c}_B S_{AB}$$
$$n_B = 2\bar{c}_B^2 + 2\bar{c}_A\bar{c}_B S_{AB} \qquad \text{(II.9)}$$

where the electronic charge has been partitioned in a Mulliken type analysis. $\overline{C}_A$ and $\overline{C}_B$ are coefficients on non-orthogonal A.O.s and S_{AB} is the overlap integral. In either case

$$n_A + n_B = 2 .$$

APPENDIX III. The program "SIGSOLVE"

This program is written in Algol 60 and is designed for use on the Elliott 4130 computer at the University of Warwick.

The program sets up and solves matrices like equation (3·8) for molecules containing a range of bond types.

Procedure SIGMAT

This procedure sets up the sigma charge matrix. The topological structure of the molecule is input in terms of pairs of atoms. The program sorts out the ordering of the atoms in any pair so that it is the same as the ordering for which the bond parameters have been evaluated. For example, parameters for the C(te) - N(te) bond are evaluated for the case in which C(te) is the first atom of the bond, not the second one. Bonds consisting of the following atoms are dealt with

C(te)	S(2p)
N(te)	H(1s)
N(2p)	Cl (3p)
O(te)	Cl (S=0·2)
O(2p)	F(2p)
S(te)	

(The symbols in brackets indicate the type of orbital used by the atom in bond formation).

The procedure next works out the elements of the sigma matrix ready for the next stage which is governed by the procedure SOLUTION.

Procedure SOLUTION

This procedure diagonalises the sigma charge matrix. Finally the orbital charges are obtained as the right hand side of the matrix equation.

Input data

TAN	-	total number of atoms
NB	-	number of bonds
AT) PI) LP)	-	arrays giving the atom type, number of pi electrons and number of lone pair electrons of an atom.
NB	-	bond indicator array giving the topological structure of the molecule.
FX) RX)	-	standard bond parameters calculated from the completely correlated expression 3·14.

```
&END;
 ** ICL 4130 DE32 SYSTEM  :  SLAVE BIG        :  CORE 70K  :  VOL  9

&JOB;MS/R047/DE;

&LINES;10000;
SNOP
JTW 26DC
BATCH

&ALGOL;L;
LIBRARY
ALGOL

    1   SIGSOLVE;
    2   "BEGIN"
    3   "COMMENT"   THIS PROGRAM SETS UP SIGMA MATRIX AND SOLVES IT FOR
    4   SIGMA-BONDED MOLECULES;
    5   "INTEGER"MM,I,J,K,N,TAN,BN;
    6   "REAL"RHOO,EON;
    7   "INTEGER""ARRAY"HEAD[1:15];
    8   MM:=1;
    9   INSTRING(HEAD,MM);
   10   "PRINT"'/'FL5S45'SIGMA CHARGE CALCULATION FOR   ';
   11   MM:=1;
   12   OUTSTRING(HEAD,MM);
   13   "READ"N,TAN;
   14   "BEGIN"
   15   "ARRAY"RX[1:14,1:14],FX[1:11,1:14],XX[1:N];
   16   "ARRAY"AA[1:N,1:N+1];
   17   "INTEGER""ARRAY"PI,AT,LP[1:TAN],
   18          NB[1:TAN,1:TAN];
   19   "PROCEDURE"SIGMAT(N,TAN,AA,RX,FX,PI,AT,LP,NB);
   20   "VALUE"N,TAN;
   21   "INTEGER"N,TAN;
   22   "ARRAY"AA,RX,FX;
   23   "INTEGER""ARRAY"AT,LP,NB,PI;
   24   "BEGIN""INTEGER"I,J,K,BOND,X,Y,P,Q,MULT1,MULT2;
   25   "INTEGER""ARRAY"MATOM[1:2,1:N];
   26   "FOR"I:=1"STEP"1"UNTIL"TAN-1"DO"
   27   "FOR"J:=I+1"STEP"1"UNTIL"TAN"DO"
   28   "IF"NB[I,J]=1"THEN"
   29   "BEGIN"
   30   "IF"AT[I]=1"THEN""GOTO"L6"ELSE"
   31   "IF"AT[J]=1"THEN""GOTO"L9"ELSE"
   32   "IF"AT[I]=2"THEN""GOTO"L6"ELSE"
   33   "IF"AT[I]=4"THEN""GOTO"L8"ELSE"
   34   "IF"AT[I]=7"THEN""GOTO"L9"ELSE"
   35   "IF"AT[I]=6"THEN""GOTO"L6"ELSE"
   36   "IF"AT[J]=4"THEN""GOTO"L9"ELSE"
   37   "IF"AT[I]=5"THEN""GOTO"L6"ELSE"
   38   "IF"AT[J]=5"THEN""GOTO"L9"ELSE"
   39   "BEGIN"   "PRINT"'/'L2S10'NEVER LEAVE A STONE UNTURNED';
   40   "GOTO"TERM;          "END";
```

```
L6:   "BEGIN""IF"AT[J]=12"OR"AT[J]=14"THEN"
NB[J,I]:=0.0"ELSE"NB[J,I]:=-NB[I,J];
"GOTO"TERM;    "END";
L9:   "BEGIN"   NB[I,J]:=-NB[I,J];  NB[J,I]:=1;   "GOTO"TERM;  "END";
TERM:   "END";

BDNO:=0;
"FOR"I:=1"STEP"1"UNTIL"TAN"DO"
"FOR"J:=1"STEP"1"UNTIL"TAN"DO"
"IF"NB[I,J]=1"THEN""BEGIN"BDNO:=BDNO+1;
MATOM[1,BDNO]:=I;
MATOM[2,BDNO]:=J;
"END";
BDNO:=0;
"FOR"I:=1"STEP"1"UNTIL"TAN"DO"
"FOR"J:=1"STEP"1"UNTIL"TAN"DO"
"BEGIN""IF"NB[I,J]=1"THEN"
"BEGIN"   BDNO:=BDNO+1;   X:=Y:=0;
"FOR"K:=1"STEP"1"UNTIL"N"DO"
"BEGIN"    P:=MATOM[1,K];   Q:=MATOM[2,K];
"IF"I=P"AND"J=0"THEN"
AA[BDNO,K]:=AA[BDNO,K]
"ELSE"   "BEGIN"  "IF"P=J"THEN"MULT1:=NB[Q,0]
"ELSE""IF"Q=J"THEN"MULT1:=NB[Q,P]
"ELSE"MULT1:=0;
"IF"P=I"THEN"MULT2:=NB[P,0]"ELSE""IF"Q=I"THEN"MULT2:=NB[Q,P]
"ELSE"MULT2:=0;
AA[BDNO,K]:=AA[BDNO,K]-RX[AT[J],AT[I]]*MULT1+RX[AT[I],AT[J]]*MULT2;
"END";

"IF"Q=J"AND"I"NE"P"THEN"X:=X+2;
"IF"Q=I"AND"J"NE"P"THEN"Y:=Y+2;
"END";
            AA[BDNO,N+1]:=  RX[AT[I],AT[J]]+(PI[J]+LP[J]+X)
*RX[AT[J],AT[I]]-(PI[I]+LP[I]+Y)*RX[AT[I],AT[J]];
"END";
"END";
"END";

"PROCEDURE"SOLUTION(A,N,X);
    "VALUE"N;
      "INTEGER"N;
"ARRAY"A,X;
"BEGIN"
      "INTEGER"K,I,J,L,M,P,Q,INT,T,S;
      "REAL"RR,DET;
      "ARRAY"G,F[1:N,1:N+1],R,REV[1:N];
      "INTEGER""ARRAY"B[1:N];
        K:=0;
      "PRINT"(''L2'INITIAL  MATRIX');
        "FOR"I:=1"STEP"1"UNTIL"N"DO"
"BEGIN""  PRINT"(''L2'');
        B[I]:=I;
        "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
"BEGIN"
        F[I,J]:=A[I,J];
        G[I,J]:=A[I,J];
        "COMMENT"ELEMENTS OF G[I,J] ARE NOT DESTROYED
                THROUGHOUT PROGRAMME;
        "PRINT"SAMEL'NL,A[I,J]
```

```
101   "END";
102   "END";
103             RECYCLE:
104             L:=0;
105             N:=0;
106             RR:=0;
107             RETURN;
108             N:=N+1;
109             P:=N;
110             Q:=N;
111             "FOR"I:=N"STEP"1"UNTIL"N"DO"
112             "FOR"J:=N"STEP"1"UNTIL"N"DO"
113   "BEGIN"   "IF"ABS(A[I,J])>ABS(A[P,Q])
114             "THEN"
115   "BEGIN"   P:=I;
116             Q:=J
117   "END";
118   "END";
119             INT:=B[N];
120             B[N]:=B[Q];
121              B[Q]:=INT;
122             "FOR"I:=1"STEP"1"UNTIL"N"DO"
123   "BEGIN"       A[I,Q]:=F[I,N];
124                  F[I,M]:=F[I,Q];
125                   A[I,N]:=F[I,M];
126                   F[I,Q]:=A[I,Q]
127   "END";
128             "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
129   "BEGIN"           A[M,J]:=A[P,J];
130                     A[P,J]:=F[M,J];
131                     F[M,J]:=A[M,J];
132                     F[P,J]:=A[P,J]
133   "END";
134             "IF"L=N-1
135             "THEN"
136   "BEGIN"   T:=N+1;
137             REPEAT:
138              "IF"T=2
139             "THEN"
140   "BEGIN"   "PRINT"
141         ''L2'',SAMELINE,'RESULTS(',DIGITS(3),K,')'S1'',SAMELINE,
142                                                 'RESIDUAL CYCLE(S))';
143             "FOR"I:=1"STEP"1"UNTIL"N"DO"
144   "BEGIN"   X[I]:=A[I,N+1]/A[I,I];
145   REV[I]:=X[I];
146   "END";
147   "FOR"I:=1"STEP"1"UNTIL"N"DO"
148   X[B[I]]:=REV[I];
149   "FOR"I:=1"STEP"1"UNTIL"N"DO"
150             "PRINT"''L2'',SAMELINE,'X[',DIGITS(3), I   ,']=',X[I];
151             "GOTO"FINISH;
152   "END"
153             "ELSE"
154   "BEGIN"
155             T:=T-1;
156             "FOR"I:=T-1"STEP"-1"UNTIL"1"DO"
157             "FOR"J:= T "STEP" 1"UNTIL"N+1"DO"
158             A[I,J]:=A[I,J]-(F[I,T]*F[T,J]/F[T,T]);
159             "FOR"I:=T-1"STEP"-1"UNTIL"1"DO"
160             "FOR"J:=T"STEP"1"UNTIL"N+1"DO"
```

```
161             F[I,J]:=A[I,J]
162     "END";
163             "GOTO"REPEAT;
164     "END"
165             "ELSE"
166     "BEGIN" L:=L+1;
167             "FOR"I:=L+1"STEP"1"UNTIL"N"DO"
168             "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
169             A[I,J]:=A[I,J]-((F[I,L]*F[L,J])/F[L,L])
170     "END";
171             "FOR"I:=1"STEP"1"UNTIL"N"DO"
172             "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
173             F[I,J]:=A[I,J];
174             "GOTO"RETURN;
175             FINISH;
176             "PRINT"
177             DIGITS(3),K,''S1'',SAMELINE,'RESIDUAL CYCLE(S))';
178             "FOR"I:=1"STEP"1"UNTIL"N"DO"
179     "BEGIN"
180             "PRINT"''L2'';
181             "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
182             "PRINT"SAMELINE,A[I,J];
183     "END";
184     DET:=A[1,1];
185     "FOR"I:=2"STEP"1"UNTIL"N"DO"
186     DET:=DET*A[I,I];
187     "PRINT"''L2'',SAMELINE,'DETERMINANT=',DET;
188             "PRINT"
189             ''L2''   RESIDUALS(',SAMELINE,DIGITS(3),K,''S1'',SAMELINE,
190                                                 'RESIDUAL CYCLE(S))';
191             "FOR"I:=1"STEP"1"UNTIL"N"DO"
192     "BEGIN"
193             R[I]:=0;
194             "FOR"J:=1"STEP"1"UNTIL"N"DO"
195     "BEGIN" R[I]:=R[I]+X[J]*G[I,J];
196             A[I,J]:=G[I,J];
197             F[I,J]:=A[I,J];
198     "END";
199     "END";
200             "FOR"I:=1"STEP"1"UNTIL"N"DO"
201     "BEGIN" R[I]:=R[I]-G[I,N+1];
202             "PRINT"''L2'',SAMELINE,'R[',DIGITS(3),I,']=',R[I];
203             "IF"ABS(R[I])>0,00000001
204             "THEN"RR:=R[I]
205     "END";
206             "IF"ABS(RR)>0,00000001
207             "THEN""GOTO"RESIDUAL
208             "ELSE""GOTO"COMPLETE;
209             RESIDUAL;
210             K:=K+1;
211             "IF"K=3
212             "THEN""GOTO"COMPLETE
213             "ELSE"
214     "BEGIN" "FOR"I:=1"STEP"1"UNTIL"N"DO"
215     "BEGIN" A[I,N+1]:=G[I,N+1]-R[I];
216             F[I,N+1]:=A[I,N+1];
217             B[I]:=I
218     "END";
219     "END";
220             "GOTO"RECYCLE;
```

```
            COMPLETE;
    "END";

          FREEPOINT(6);
          SPECIAL(5);
          SAMELINE;

    "COMMENT" INPUT OF BOND DATA;

    "BEGIN"
    "FOR"I:=1"STEP"1"UNTIL"N"DO"
    "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
    "BEGIN""IF"I=J"THEN"AA[I,J]:=1,0"ELSE"AA[I,J]:=0.0;     "END";

    "FOR"I:=1"STEP"1"UNTIL"TAN"DO"
    "FOR"J:=1"STEP"1"UNTIL"TAN"DO"
    NB[I,J]:=0;

    "FOR"I:=1"STEP"1"UNTIL"TAN-1"DO"
    "FOR"J:=I+1"STEP"1"UNTIL"TAN"DO"
    "READ"NB[I,J];

    "FOR"I:=1"STEP"1"UNTIL"14"DO"
    "FOR"J:=1"STEP"1"UNTIL"14"DO"
    "READ"RX[I,J];
    "FOR"I:=1"STEP"1"UNTIL"14"DO"
    "BEGIN""PRINT"''L2'';
    "FOR"J:=1"STEP"1"UNTIL"14"DO"
    "PRINT"SAMELINE,RX[I,J];
    "END";

    "FOR"I:=1"STEP"1"UNTIL"11"DO"
    "FOR"J:=I"STEP"1"UNTIL"14"DO"
    "READ"FX[I,J];
    "FOR"I:=1"STEP"1"UNTIL"11"DO"
    "BEGIN""PRINT"''L2'';
    "FOR"J:=I"STEP"1"UNTIL"14"DO"
    "PRINT"SAMELINE,FX[I,J];
    "END";

    "FOR"I:=1"STEP"1"UNTIL"TAN"DO"
    "READ"AT[I],PI[I],LP[I];
    "BEGIN""PRINT"''L2'';
    "FOR"I:=1"STEP"1"UNTIL"TAN"DO"
    "PRINT"AT[I],SAMELINE,PI[I],LP[I];
    "END";
    "END";
              SIGMAT(N,TAN,AA,RX,FX,PI,AT,LP,NB);
    SOLUTION(AA,N,XX);

    "COMMENT"NOW COMES CALCULATION OF N.Q.R. FREQUENCIES;
    "PRINT"''L2S35'NQR FREQUENCIES IN MC/S';
    "PRINT"''L2S6'CL ATOM'S10'N[QCL]'S10'RHOO 'S10'EQN. MC/S';
    BN:=0;
    "FOR"I:=1"STEP"1"UNTIL"TAN"DO"
    "FOR"J:=1"STEP"1"UNTIL"TAN"DO"
    "IF"NB[I,J]=1"THEN""BEGIN"BN:=BN+1;
    "IF"AT[J]=14"THEN""BEGIN"RHOO:=XX[BN]*0,8;      EQN:=54,873*RHOO;
    "PRINT"''L1S10'',J,SAMELINE,''S6'',XX[BN],''S6'',RHOO,''S6'',EQN;
    "END";"END";
```

```
  231    "END";"END";
   480      MC
  1966   CODE
  2446  TOTAL


 &DIAG;
DIAG


 &RUN;
SIGSOLVE
DRO
```

APPENDIX IV. The main PPP ($\sigma + \pi$) program.

This program is written in Algol 60. It consists of a preliminary calculation of the sigma charges in the molecule using procedures SIGMAT and SOLUTION (see appendix III) although the number of atoms which can be treated is extended.

The range of atom types parametrised for is as follows

C(tr)	$\ddot{O}$(tr)
C(te)	S(te)
N(te)	H(1s)
$\dot{N}$(tr)	F(2p)
$\ddot{N}$(tr)	Cl(3p)
O(te)	F(tr)
$\dot{O}$(tr)	Cl(tr)

The actual range of bond types which can be treated is given in chapter 4.

The sigma charges are used to calculate the VSIP's and the δ_{ii}. The VSIP's, γ_{ii}'s and δ_{ij}'s are recalculated prior to each new cycle of the PPP computation in response to changes in the pi electron distribution.

Library procedure EIGENSOLVE

This procedure diagonalises the PPP Hamiltonian matrix. During the process the procedure SYMMETRIC QR2 is called. The eigenvalues and eigenvectors are passed on to the procedure SORTOUT.

Procedure SORTOUT

This procedure places the eigenvalues in the order of increasing energy. The eigenvectors are altered correspondingly. The one electron energies and the coefficients are printed. The elements are retained for use in the procedures MCLACHLAN and PIPROPS.

Procedure MCLACHLAN

This procedure computes the PPP and McLachlan spin densities and prints them.

Procedure PIPROPS

This procedure computes the pi electron properties of the molecule. Pi electron charges, bond orders and total pi electron energy are computed and printed.

Termination of computation

The computation finishes when the differences between the n^{th} and $(n-1)^{th}$, and n^{th} and $(n-2)^{th}$ computed values of the pi electron energy respectively are both less than 10^{-5} eV.

Valence state ionisation potentials, VSIP's.

The equations used in the program are presented in table IV. 1

ATOM	VSIP eV		
C(tr tr tr π)[a]	11·254	+4·909Q_c	+0·451Q_c^2
N(tr tr tr $^2\pi$)[a]	14·214	+5·825Q_N	+0·430Q_N^2
N(tr tr tr π^2)[b]	28·709	+16·849Q_N	+1·894Q_N^2
O(tr tr tr$^2\pi^2$)[b]	34·946	+18·265Q_o	+1·665Q_o^2

a. The derivation of these equations is discussed in chapter 7.

b. These equations are taken from the valence state data of Hinze, Jaffe and coworkers[19,20].

TABLE IV. 1. VSIP EQUATIONS USED IN THE PROGRAM.

One-and two-centre repulsion integrals γ_{ii} and γ_{ij} :

The parametric equations used to compute the one-centre repulsion integrals, γ_{ii}, are given in table IV.2.

ATOM	γ_{ii} eV
C(tr tr tr π)[a]	$11{\cdot}282 + 1{\cdot}1530_C$
N(tr tr tr$^2\pi$)[a]	$12{\cdot}846 + 1{\cdot}1530_N$
N(tr tr tr π^2)[b]	$16{\cdot}756 + 4{\cdot}3960_N - 0{\cdot}3880_N^2$
O(tr tr tr$^2\pi^2$)[b]	$17{\cdot}654 + 1{\cdot}4620_O - 0{\cdot}6040_O^2$

a. The derivation of these equations is discussed in chapter 7.

b. The VSEA of the atom is computed as well as the VSIP, on each cycle, and the Pariser-Parr approximation is used[18],

$$\gamma_{ii} = I_i - A_i \qquad \text{(IV.1)}$$

TABLE IV. 2 γ_{ii} EQUATIONS USED IN THE PROGRAM

The two-centre repulsion integrals, γ_{ij}, for all atoms are computed from the Beveridge - Hinze expression[94].

$$\gamma_{ij} = 1/ (a \exp(- r_{ij}^2 / 2a^2) + r_{ij}) \qquad \text{(IV.2)}$$

where

$$a = 2/ (\gamma_{ii} + \gamma_{jj}) \qquad \text{(IV.3)}$$

In their paper the γ_{ii} are in hartrees and the bond lengths, r, are in bohrs so that the γ_{ij} are obtained in atomic units. In the present work the γ_{ij} are converted from atomic units into eV.

INPUT DATA

The input data for the program is made up as follows:-

LAMDA - McLachlan parameter.

NNO - number of pi electrons.

ATOM NO - number of atoms taking part in pi electron system.

BOND NO - number of pielection bonds.

ITNO - number of iterations of the PPP calculations.

N - number of sigma bonds.

NUNIT - number of two electron integrals.

TAN - total number of atoms.

(TITLE) - name of molecule.

NB(I,J) - sigma bond indicators for atoms I and J.

FK (I, J) - sigma bond k parameters for bond I - J.

FK (I, J) - sigma bond I parameters for bond I - J.

AT (I) - type of atom I.

PT (I) - number of pi electrons on atom I.

LP (I) - number of lone pair electrons on atom I.

BETA (I,J) - β values in eV for pi bond I - J.

RA (I,J) - length of bond I–J in angstrom units.

INPUT FOR FURAN

As an example, the actual input data for furan are listed below

```
0·75      6   5   5   20   9   3   10   9   ' FURAN '
1   0     0   1   0   0    0   0   )
    1     0   0   1   0    0   0   )
          1   0   0   1    0   0   )
                                   )
              1   0   0    1   0   )
                  0   0    0   1   )
                      0    0   0   )
                           0   0   )
                               0   )
```

SIGMA BOND PARAMETERS - STANDARD DATA

```
8   2   2   )
1   1   0   )
1   1   0   )
1   1   0   )
1   1   0   )
1   1   0   )
12  0   0   )
12  0   0   )
12  0   0   )
12  0   0   )
```

```
1   2   -2·50   2   3   -2·39   3   4   -2·39   4   5   -2·39   )
                  5   1   -2·39                                 )
```

```
1·37   2·24   2·24   1·37   1·35   2·23   2·19   1.44   2·23   1·35
```

```
** ICL 4130 DOS2 SYSTEM  :  SLAVE BACK      :  CORE 46K  :  VOL  9


&JOB;MS/R04//S1;


&ALGOL;L;
LIBRARY
ALGOL


&LINES;  1000000;


&LIST;

   1    ITERATIVE PROGRAM FOR CHARGES;
   2    "BEGIN"
   3
   4    "COMMENT"
   5          THIS PROGRAM PERFORMS ITERATIVE SIGMA-PI CALCULATIONS,IT COMP
   6          CHARGES,FREE VALENCES,PPP AND MCLACHLAN SPIN DENSITIES, ONE-
   7          ELECTRON ENERGIES,TOTAL PI ENERGY AND BOND ORDERS;
   8    "INTEGER"M,END,ATOM NO,BOND NO,I,J,N,K,P,U,V,ITNO,X,Y,W,OCC,
   9             COUNT,NINT,TAN;
  10    "REAL"LAMDA,SUMX,H;
  11    "READ"LAMDA,END,ATOM NO,BOND NO,ITNO,N,OCC,NINT,TAN;
  12    "BEGIN"
  13    "ARRAY"F,SS,BETA,BOI,ROC,GAMMA,CC,COEFF[1:ATOM NO,1:ATOM NO],
  14       VSIP,QC,MON,Z[1:ATOM NO],AA,ACC[1:N,1:N+1],AX,RA,RRE[1:ATOM NO,
  15    1:ATOM NO],PI[1:TAN],RX[1:17,1:17],FX[1:9,1:17],VSEA[1:ATOM NO],
  16    XX[1:N],STORE[1:ITNO],FCC[1:ATOM NO,1:ATOM NO];
  17    "ARRAY"PII[1:ATOM NO,1:ITNO],XXI[1:N,1:ITNO];
  18    "INTEGER""ARRAY"HEAD[1:15],BONDS[1:2,1:BOND NO],BONDD[1:2,1:NINT],
  19                    AT,LP[1:TAN],NBC[1:TAN,1:TAN];
  20    "PROCEDURE"SOLUTION(A,N,X);
  21          "VALUE"N;
  22          "INTEGER"N;
  23          "ARRAY"A,X;
  24    "BEGIN"
  25          "INTEGER"K,I,J,L,M,P,Q,INT,T,S;
  26          "REAL"PR,DET;
  27          "ARRAY"G,CC[1:N,1:N+1],R,REV[1:N];
  28          "INTEGER""ARRAY"B[1:N];
  29            K:=0;
  30          "PRINT"//L2'INITIAL  MATRIX';
  31            "FOR"I:=1"STEP"1"UNTIL"N"DO"
  32    "BEGIN""  PRINT"//L2'';
  33            B[I]:=I;
  34            "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
  35    "BEGIN"
  36            CC[I,J]:=A[I,J];
  37            G[I,J]:=A[I,J];
  38            "COMMENT"ELEMENTS OF G[I,J] ARE NOT DESTROYED
  39                     THROUGHOUT PROGRAMME;
  40            "PRINT"SAMELINE,A[I,J]
```

```
41    "END";
42    "END";
43              RECYCLE:
44              L:=0;
45              M:=0;
46              BB:=0;
47              RETURN:
48              M:=M+1;
49              P:=M;
50              Q:=M;
51              "FOR"I:=M"STEP"1"UNTIL"N"DO"
52              "FOR"J:=M"STEP"1"UNTIL"N"DO"
53    "BEGIN"   "IF"ABS(A[I,J])>ABS(A[P,Q])
54              "THEN"
55    "BEGIN"   P:=I;
56              Q:=J
57    "END";
58    "END";
59              INT:=B[M];
60              B[M]:=B[Q];
61               B[Q]:=INT;
62              "FOR"I:=1"STEP"1"UNTIL"N"DO"
63    "BEGIN"       A[I,Q]:=F[I,M];
64                   F[I,M]:=F[I,Q];
65                     A[I,M]:=F[I,M];
66                     F[I,Q]:=A[I,Q]
67    "END";
68              "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
69    "BEGIN"           A[M,J]:=A[P,J];
70                      A[P,J]:=F[M,J];
71                      F[M,J]:=A[M,J];
72                      F[P,J]:=A[P,J]
73    "END";
74              "IF"L=N-1
75              "THEN"
76    "BEGIN"   T:=M+1;
77              REPEAT:
78               "IF"T=2
79              "THEN"
80    "BEGIN"   "PRINT"
81           (''L2'',SAMELINE,'RESULTS(',DIGITS(3),K,''S1'',SAMELINE,
82                                                  'RESIDUAL CYCLE(S))');
83              "FOR"I:=1"STEP"1"UNTIL"N"DO"
84    "BEGIN"   X[I]:=A[I,N+1]/A[I,I];
85    REV[I]:=X[I];
86    "END";
87    "FOR"I:=1"STEP"1"UNTIL"N"DO"
88    X[B[I]]:=REV[I];
89    "FOR"I:=1"STEP"1"UNTIL"N"DO"
90              "PRINT"(''L2'',SAMELINE,'X(',DIGITS(3), I  ,')=',X[I]);
91              "GOTO"FINISH;
92    "END"
93              "ELSE"
94    "BEGIN"
95              T:=T-1;
96              "FOR"I:=T-1"STEP"-1"UNTIL"1"DO"
97              "FOR"J:= T "STEP" 1"UNTIL"N+1"DO"
98              A[I,J]:=A[I,J]-(F[I,T]*F[T,J]/F[T,T]);
99              "FOR"I:=T-1"STEP"-1"UNTIL"1"DO"
100             "FOR"J:=T"STEP"1"UNTIL"N+1"DO"
```

```
101             F[I,J]:=A[I,J]
102     "END";
103             "GOTO"REPEAT;
104     "END"
105             "ELSE"
106     "BEGIN" L:=L+1;
107             "FOR"I:=L+1"STEP"1"UNTIL"N"DO"
108             "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
109             A[I,J]:=A[I,J]-((F[I,L]*F[L,J])/F[L,L])
110     "END";
111             "FOR"I:=1"STEP"1"UNTIL"N"DO"
112             "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
113             F[I,J]:=A[I,J];
114             "GOTO"RETURN;
115             FINISH:
116             "PRINT"
117             ('L2')   REDUCED ROW ECHELON MATRIX (',SAMELINE,
118             DIGITS(3),K,(''S1''),SAMELINE,'RESIDUAL CYCLE(S))');
119             "FOR"I:=1"STEP"1"UNTIL"N"DO"
120     "BEGIN"
121             "PRINT"('L2');
122             "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
123             "PRINT"SAMELINE,A[I,J];
124     "END";
125     DET:=A[1,1];
126     "FOR"I:=2"STEP"1"UNTIL"N"DO"
127     DET:=DET*A[I,I];
128     "PRINT"('L2'),SAMELINE,'DETERMINANT=',DET;
129             "PRINT"
130             ('L2')   RESIDUALS(',SAMELINE,DIGITS(3),K,(''S1''),SAMELINE,
131                                                     'RESIDUAL CYCLE(S))');
132             "FOR"I:=1"STEP"1"UNTIL"N"DO"
133     "BEGIN"
134             R[I]:=0;
135             "FOR"J:=1"STEP"1"UNTIL"N"DO"
136     "BEGIN" R[I]:=R[I]+X[J]*G[I,J];
137             A[I,J]:=G[I,J];
138             F[I,J]:=A[I,J];
139     "END";
140     "END";
141             "FOR"I:=1"STEP"1"UNTIL"N"DO"
142     "BEGIN" R[I]:=R[I]-G[I,N+1];
143             "PRINT"('L2'),SAMELINE,('R('),DIGITS(3),I,(')='),R[I];
144             "IF"ABS(R[I])>0.00000001
145             "THEN"RR:=R[I]
146     "END";
147             "IF"ABS(RR)>0.00000001
148             "THEN""GOTO"RESIDUAL
149             "ELSE""GOTO"COMPLETE;
150             RESIDUAL:
151             K:=K+1;
152             "IF"K=3
153             "THEN""GOTO"COMPLETE
154             "ELSE"
155     "BEGIN" "FOR"I:=1"STEP"1"UNTIL"N"DO"
156     "BEGIN" A[I,N+1]:=G[I,N+1]-R[I];
157             F[I,N+1]:=A[I,N+1];
158             B[I]:=I
159     "END";
160     "END";
```

```
161             "GOTO"RECYCLE;
162             COMPLETE;
163     "END";
164
165     "PROCEDURE"SIGNAT(N,TAN,COUNT,AA,PI,RX,FX,AT,LP,NB);
166     "VALUE"N,TAN,COUNT;
167     "INTEGER"N,TAN,COUNT;
168     "ARRAY"AA,PI,RX,FX;
169     "INTEGER""ARRAY"AT,LP,NB;
170     "BEGIN""INTEGER"I,J,K,BDNO,X,Y,P,Q,MULT1,MULT2;
171     "INTEGER""ARRAY"MATOM[1:2,1:N];
172     "FOR"I:=1"STEP"1"UNTIL"TAN-1"DO"
173     "FOR"J:=I+1"STEP"1"UNTIL"TAN"DO"
174     "IF"NB[I,J]=1"THEN"
175     "BEGIN"
176     "IF"AT[I]=1"THEN""GOTO"L8"ELSE"
177     "IF"AT[J]=1"THEN""GOTO"L9"ELSE"
178     "IF"AT[I]=2"THEN""GOTO"L3"ELSE"
179     "IF"AT[I]=4"THEN""GOTO"L8"ELSE"
180     "IF"AT[I]=8"THEN""GOTO"L9"ELSE"
181     "IF"AT[I]=5"THEN""GOTO"L8"ELSE"
182     "IF"AT[J]=5"THEN""GOTO"L9"ELSE"
183     "BEGIN"    "PRINT"(*L2S10'NEVER LEAVE A STONE UNTURNED');
184     "GOTO"TERM;              "END";
185     L8:    "BEGIN""IF"AT[J]=12"THEN"NB[J,I]:=0,0"ELSE"NB[J,I]:=-NB[I,J]
186     "GOTO"TERM;     "END";
187     L9:    "BEGIN"    NB[I,J]:=-NB[I,J];   NB[J,I]:=1;    "GOTO"TERM;  "EN
188     TERM:    "END";
189
190     BDNO:=0;
191     "FOR"I:=1"STEP"1"UNTIL"TAN"DO"
192     "FOR"J:=1"STEP"1"UNTIL"TAN"DO"
193     "IF"NB[I,J]=1"THEN""BEGIN"BDNO:=BDNO+1;
194     MATOM[1,BDNO]:=I;
195     MATOM[2,BDNO]:=J;
196     "END";
197     BDNO:=0;
198     "FOR"I:=1"STEP"1"UNTIL"TAN"DO"
199     "FOR"J:=1"STEP"1"UNTIL"TAN"DO"
200     "BEGIN""IF"NB[I,J]=1"THEN"
201     "BEGIN"    BDNO:=BDNO+1;    X:=Y:=0;
202     "FOR"K:=1"STEP"1"UNTIL"N"DO"
203     "BEGIN"    P:=MATOM[1,K];    Q:=MATOM[2,K];
204     "IF"COUNT>1"THEN""GOTO"L10"ELSE"
205     "BEGIN""IF"I=P"AND"J=Q"THEN"
206     AA[BDNO,K]:=AA[BDNO,K]
207     "ELSE"    "BEGIN"    "IF"P=J"THEN"MULT1:=NB[P,Q]
208     "ELSE""IF"Q=J"THEN"MULT1:=NB[Q,P]
209     "ELSE"MULT1:=0;
210     "IF"P=I"THEN"MULT2:=NB[P,Q]"ELSE""IF"Q=I"THEN"MULT2:=NB[Q,P]
211     "ELSE"MULT2:=0;
212     AA[BDNO,K]:=AA[BDNO,K]-RX[AT[J],AT[I]]*MULT1*RX[AT[I],AT[J]]*MULT2;
213     "END";
214
215     L10:    "BEGIN"
216     "IF"Q=J"AND"I"NE"P"THEN"X:=X+2;
217     "IF"P=I"AND"J"NE"P"THEN"Y:=Y+2;
218     "END";
219     "END";
220     "END";
```

```
221                AA[RDNO,N+1]:=  FX[AT[I],AT[J]]+(PI[J]+LP[J]+X)
222    *RX[AT[J],AT[I]]-(PI[I]+LP[I]+Y)*RX[AT[I],AT[J]];
223    "END";
224    "END";
225    "END";
226
227    "PROCEDURE"COPYMX(ONE,TWO,THREE,FOUR);
228           "VALUE"THREE,FOUR;
229    "INTEGER"THREE,FOUR;
230           "ARRAY"ONE,TWO;
231    "BEGIN"
232           "INTEGER"I1,I2;
233           "FOR"I1:=1"STEP"1"UNTIL"THREE"DO"
234           "FOR"I2:=1"STEP"1"UNTIL"FOUR"DO"
235           TWO[I1,I2]:=ONE[I1,I2];
236    "END";
237
238
```

ITEM INSERTED

```
239    "LIBRARY" EIGENSOLVE;
242
243    "PROCEDURE"SORTOUT(CO,FX,N,MONEN,C);
244                  "VALUE"N;
245                  "INTEGER"N;
246    "ARRAY"CO,C,MONEN,FX;
247
248       "BEGIN""COMMENT"WE SORT OUT EIGENVALUES IN INCREASING ORDER,
249                        I,E, INCREASING ENERGY,AND ALTER THE EIGENVECTOR
250                        WE THEN TRANSPOSE THE COEFFICIENT MATRIX AND
251                        FINALLY TABULATE THE ONE-ELECTRON ENERGIES AND
252                        COEFFICIENTS;
253
254    •           "INTEGER"I,J,T,Q;
255                "REAL"CHANGE;
256                  "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
257    MONEN[I]:=FX[I,I];
258                  "FOR"X:=ATOM NO"STEP"-1"UNTIL"2"DO"
259                  "FOR"I:=2"STEP"1"UNTIL"X"DO"
260                    "IF"MONEN[I-1]>MONEN[I]"THEN""BEGIN"
261                      CHANGE:=MONEN[I-1];
262                      MONEN[I-1]:=MONEN[I];
263                      MONEN[I]:=CHANGE;
264                  "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO""BEGIN"
265    CHANGE:=CO[J,I-1];
266    CO[J,I-1]:=CO[J,I];
267    CO[J,I]:=CHANGE;
268       "END";
269       "END";
270    "COMMENT" NOW TRANSPOSE;
271                  "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
272                  "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
273    C[I,J]:=CO[I,J];
274                  "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
275                  "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
```

```
276   CC[I,J]:=CC[J,I];
277
278      "BEGIN""COMMENT"NOW PRINT ONE-ELECTRON ENERGIES AND COEFFICIENTS
279                      10 COLUMNS WITH HEADINGS;
280                "FOR"Q:=1"STEP"10"UNTIL"N"DO"
281                   "BEGIN"T:="IF"N-Q<10"THEN"N"ELSE"Q+9;
282                      "PRINT"(/L2S30'ONE-ELECTRON ENERGIES I N
283                            ASCENDING ORDER'L2');
284                         "FOR"I:=Q"STEP"1"UNTIL"T"DO"
285                      "PRINT"PREFIX(''S2''),MONEN[I];
286                      "PRINT"(/L3S32'COEFFICIENTS IN COLUMNS'L2');
287                         "FOR"I:=1"STEP"1"UNTIL"N"DO"
288                           "BEGIN""FOR"J:=0"STEP"1"UNTIL"T"DO"
289   "PRINT"PREFIX(''S2''),CC[J,I];
290                               "PRINT"(''L'');
291                              "END";
292                      "END";
293      "END";
294      "END"OF SORTOUT;
295
296   "PROCEDURE" MCLACHLAN(AN, H, L, C, E);
297   "VALUE" AN, H, L;   "INTEGER" AN, H;   "REAL" L;   "ARRAY" C, E;
298   "COMMENT" CALCULATES AND PRINTSPPP AND MCLACHLAN SPIN
299   DENSITIES FOR ANION RADICALS WITH ANY NUMBER OF DEGENERATE
300   LOWEST ANTIBONDING ORBITALS;
301   "BEGIN" "INTEGER" X, Y, I, J, S, T;
302   "REAL" D;
303   "REAL" "ARRAY" SUMPI, SPI, PI[1:AN,1:AN], SD, SUMRHO, RHO[1:AN];
304   "FOR" X:=1 "STEP" 1 "UNTIL" AN "DO"
305   "FOR" Y:=1 "STEP" 1 "UNTIL" AN "DO" "BEGIN"
306   SPI[X,Y]:=0.0;
307   "FOR" J:=H+1 "STEP" 1 "UNTIL" AN "DO" "BEGIN"
308   SUMPI[X,Y]:=0.0;
309   "FOR" I:=1 "STEP" 1 "UNTIL" H "DO"
310   SUMPI[X,Y]:=SUMPI[X,Y]+((CC[I,X]*CC[I,Y])/(EC[J]-EC[I]));
311   SPI[X,Y]:=SPI[X,Y]+SUMPI[X,Y]*(CC[J,X]*CC[J,Y]);   "END";
312   PI[X,Y]:=-(4*SPI[X,Y]);   "END";
313   "FOR" X:=1 "STEP" 1 "UNTIL" AN "DO" "BEGIN"
314   S:=1;   T:=H+1;
315   D:=CC[T,X]↑2;
316   SDIN:   T:=T+1;
317   "IF" ABS(EC[T]-EC[T-1])<1.0-3 "THEN" "GOTO" DENIN "ELSE" "GOTO" SPIND;
318   DENIN;   D:=D+CC[T,X]↑2;   S:=S+1;   "GOTO" SDIN;
319   SPIND;   D:=D/S;   SD[X]:=D;   "END";
320   "FOR" X:=1 "STEP" 1 "UNTIL" AN "DO" "BEGIN"
321   SUMRHO[X]:=0.0;
322   "FOR" Y:=1 "STEP" 1 "UNTIL" AN "DO"
323   SUMRHO[X]:=SUMRHO[X]+(PI[X,Y]*SD[Y]);
324   RHO[X]:=SD[X]+(L*SUMRHO[X]);   "END";
325   "PRINT" (/L2S20'ATOM'S14'SPIN DENSITIES'L1');
326   "PRINT" (/S35'PPP'S9'MCLACHLAN'L2');
327   "FOR" X:=1 "STEP" 1 "UNTIL" AN "DO"
328   "PRINT" (/S14'', SAMELINE, X, /S6'', PREFIX(''S2''), SD[X],
329   /S6'', PREFIX(''S2''), RHO[X], /L1'');
330   "END" OF MCLACHLAN;
331
332   "PROCEDURE"PIPROPS(BO,NI,BD,CF,R,PIA,ATN,G,BT,Z,STORE,V,COUNT);
333         "VALUE"NI,ATN,R,COUNT;
334      "INTEGER"NI,ATN,R,COUNT;
335   "ARRAY"BO,V,CF,PIA,STORE,G,BT,Z;
```

```
336         "INTEGER""ARRAY"BD;
337           "BEGIN"
338             "INTEGER"I,J,K,P;
339             "REAL"B,C,D,SUMA,SUMB,SUMC;
340            "COMMENT"CALCULATION OF BOND ORDERS;
341            "PRINT"(/L6S40'BOND ORDERS');
342            "PRINT"(/L2S20'BOND'S24'BOND ORDER');
343              "FOR"I:=1"STEP"1"UNTIL"NI"DO"
344               "BEGIN"  K:=BD[1,I];          P:=BD[2,I];
345                   B:=0,0;
346                  "FOR"J:=1"STEP"1"UNTIL"R"DO"
347                    "BEGIN"   B:=B+2*CF[J,P]*CF[J,K]; "END";
348                      BO[K,P]:=B;
349                      BO[P,K]:=BO[K,P];
350               "END";
351   "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
352   "BEGIN"
353   "PRINT"(/L');
354   "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
355   "BEGIN"   "IF"I=J"THEN"BO[I,J]:=0,0;
356   "PRINT"SAMELINE,BO[I,J];
357   "END";   "END";
358      "COMMENT"CALCULATION OF PI DENSITIES AND FREE VALENCE;
359        "PRINT"(/L6S27'PI DENSITY AND FREE VALENCE'/L2S26'ATOM');
360        "PRINT"(/S5'DENSITY'S12'FREE VALENCE');
361         "FOR"I:=1"STEP"1"UNTIL"AIN"DO"
362   "BEGIN" C:=0,0;
363                 "FOR"J:=1"STEP"1"UNTIL"R"DO"
364   "BEGIN"
365              C:=C+2*CF[J,I]↑2;
366   "END";
367   PIA[I]:=C;
368   "PRINT"(/L1',I,PREFIX(/S4'),C;
369
370   D:=0,0;
371   "FOR"J:=1"STEP"1"UNTIL"ATN"DO"
372   "BEGIN""IF"J=I"THEN"D:=D+0,0
373   "ELSE"D:=D+BO[I,J];
374  "END";
375                    "PRINT"PREFIX(/S4'),(SQRT(3)-D),/L';
376            "END";
377        "BEGIN""COMMENT"TOTAL ENERGY;
378          SUMA:=0,0;
379           "FOR"I:=1"STEP"1"UNTIL"ATN"DO"
380   SUMA:=SUMA+ PIA[I]*(-VC[I]+0,25*PIA[I]*GC[I,I]);
381
382                "FOR"I:=1"STEP"1"UNTIL"ATN-1"DO"
383   "BEGIN" SUMB:=0,0;
384                "FOR"J:=I+1"STEP"1"UNTIL"ATN"DO"
385                     SUMB:=SUMB+BO[I,J]*BT[I,J];
386   "END";
387
388                  "FOR"I:=1"STEP"1"UNTIL"ATN-1"DO"
389   "BEGIN" SUMC:=0,0;
390                  "FOR"J:=I+1"STEP"1"UNTIL"ATN"DO"
391   SUMC:=SUMC+((PIA[I]-Z[I])*(PIA[J]-Z[J])-0,5*BO[I,J]
392                            -Z[I]*Z[J])*GC[I,J];
393   "END";
394   STORE[COUNT]:=SUMA+SUMB+0,5*SUMC;
395   "PRINT"(/L2S20'TOTAL PI ENERGY',/S6',SAMELINE,STORE[COUNT],/S2'EV'
```

```
396         "END";
397         "END"OF PIPROPS;
398
399     "BEGIN"
400     FREEPOINT(6);
401         NN:=1;
402         INSTRING(HEAD,NN);
403         "PRINT"(/L6S45'ITERATIVE CHARGE CALCULATION FOR    ',
404         NN:=1;
405         OUTSTRING(HEAD,NN);
406           "PRINT"(/L6S26'NO OF ELECTRONS',SAMELINE,ENO;
407           "PRINT"(/L2S30'NO OF ATOMS',SAMELINE,ATOM NO;
408     "PRINT"(/L2S30'TOTAL NO OF ATOMS',SAMELINE,TAN;
409     "PRINT"(/L2S30'NO OF PI BONDS',SAMELINE,BOND NO;
410     "PRINT"(/L2S30'NO OF SIGMA BONDS',SAMELINE,N;
411           "PRINT"(/L2S30'LAMBDA',SAMELINE,('S11'),LAMBA;
412
413         "COMMENT"READ IN ELEMENTS OF SIGMA MATRIX;
414     "FOR"I:=1"STEP"1"UNTIL"N"DO"
415     "FOR"J:=1"STEP"1"UNTIL"N+1"DO"
416     "BEGIN""IF"I=J"THEN"AA[I,JJ:=1,0"ELSE"AA[I,JJ:=0;0;    "END";
417
418     "FOR"I:=1"STEP"1"UNTIL"TAN"DO"
419     "FOR"J:=1"STEP"1"UNTIL"TAN"DO"
420     NB[I,JJ:=0;
421
422     "FOR"I:=1"STEP"1"UNTIL"TAN-1"DO"
423     "FOR"J:=I+1"STEP"1"UNTIL"TAN"DO"
424     "READ"NB[I,JJ;
425
426     "FOR"I:=1"STEP"1"UNTIL"17"DO"
427     "FOR"J:=1"STEP"1"UNTIL"17"DO"
428     "READ"RX[I,JJ;
429     "FOR"I:=1"STEP"1"UNTIL"17"DO"
430     "BEGIN""PRINT"(/L2');
431     "FOR"J:=1"STEP"1"UNTIL"17"DO"
432     "PRINT"SAMELINE,RX[I,JJ;
433     "END";
434
435     "FOR"I:=1"STEP"1"UNTIL"9"DO"
436     "FOR"J:=I"STEP"1"UNTIL"17"DO"
437     "READ"FX[I,JJ;
438     "FOR"I:=1"STEP"1"UNTIL"9"DO"
439     "BEGIN""PRINT"(/L2');
440     "FOR"J:=I"STEP"1"UNTIL"17"DO"
441     "PRINT"SAMELINE,FX[I,JJ;
442     "END";
443
444     "FOR"I:=1"STEP"1"UNTIL"TAN"DO"
445     "READ"AT[I],PI[I],LP[I];
446     "BEGIN""PRINT"(/L2');
447     "FOR"I:=1"STEP"1"UNTIL"TAN"DO"
448     "PRINT"AT[I],SAMELINE,PI[I],LP[I];
449     "END";
450     "COMMENT" NOW WE COPY IN ELEMENTS OF SIGMA MATRIX AND SOLVE IT;
451     SIGMAT(N,TAN,COUNT,AA,PI,RX,FX,AT,LP,NB);
452     COPYMX(AA,AC,N,N+1);
453     SOLVIO(AC,N,XX);
454     "COMMENT" WE CALCULATE NET SIGMA CHARGES AND PRINT THEM;
455       "PRINT"(/L2S40'NET ATOMIC SIGMA CHARGES');
```

```
456   QC[1]:=1-2*XX[1]+PI[1];
457   QC[2]:=XX[1]+XX[2]+XX[3]+PI[2]-4;
458   QC[6]:=QC[2];
459   QC[3]:=XX[4]+XX[5]-XX[2]+PI[3]-2;
460   QC[5]:=QC[3];
461   QC[4]:=XX[7]+XX[6]-XX[4]+PI[4]-2;
462   QC[1]:=-QC[1];
463   QC[2]:=-QC[2];
464   QC[3]:=-QC[3];
465   QC[4]:=-QC[4];
466   QC[5]:=-QC[5];
467   QC[6]:=-QC[6];
468     "PRINT"('L2S20)'ATOM'S10)'CHARGE');
469     "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
470   "PRINT"('L1S26),I,SAMELINE,('S10),QC[I];
471        "COMMENT"NOW SET ALL ELEMENTS OF H,F, MATRIX TO ZERO;
472                 "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
473                 "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
474               "BEGIN""IF"J=I"THEN"SS[I,J]:=1,0 "ELSE" SS[I,J]:=0,0;
475                     F[K,J]:=0,0;    BETA[K,J]:=0,0;
476               "END";
477        "COMMENT"NOW READ IN BETA-XY VALUES (X,Y NEAREST NEIGHBOURS)
478                 IN UNITS OF EV;
479                 "FOR"I:=1"STEP"1"UNTIL"BOND NO"DO"
480                   "BEGIN""READ"K,P;
481                         BONDS[1,I]:=K;   BONDS[2,I]:=P;
482                         "READ"BETA[K,P];
483                         BETA[P,K]:=BETA[K,P];
484                     "PRINT"('L),PREFIX(('S2)),K,P;
485                      "PRINT"PREFIX(('S4)),BETA[K,P];
486                   "END";
487             "PRINT"('L2)';
488
489   "COMMENT" NOW CALCULATE COULOMB REPULSION INTEGRALS;
490   "PRINT"('L2S8)'ATOM'S10)'VSIP);
491        "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
492   "BEGIN"
493   VSIP[I]:=11,230+4,967*QC[I]+0,417*QC[I]↑2;
494   VSIP[1]:=14,424+5,805*QC[1]+0,413*QC[1]↑2;
495   "PRINT"('L1S10),SAMELINE,('S10),VSIP[I];
496   "END";
497
498   "FOR"I:=1"STEP"1"UNTIL"ATOM NO-1"DO"
499   "FOR"J:=I+1"STEP"1"UNTIL"ATOM NO"DO"
500   "BEGIN""READ"RA[I,J];
501   RR[I,J]:=RA[I,J]*(10/5,29167);
502   "END";
503
504   "PRINT"('L2S25)'1- AND 2-CENTRE COULOMB REPULSION INTEGRALS IN EV');
505   "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
506   "BEGIN"
507   GAMMA[I,I]:=15,894-1,153*(4-QC[I]);
508   GAMMA[1,1]:=16,611-1,153*(5-QC[1]);
509   "END";
510
511   "FOR"I:=1"STEP"1"UNTIL"ATOM NO-1"DO"
512   "FOR"J:=I+1"STEP"1"UNTIL"ATOM NO"DO"
513   "BEGIN"        AX[I,J]:=54,4/(GAMMA[I,I]+GAMMA[J,J]);
514   GAMMA[I,J]:=(1/(AX[I,J]*EXP((-RR[I,J]↑2)/(2*AX[I,J]↑2))+RR[I,J]))*27,2;
515   GAMMA[J,I]:=GAMMA[I,J];
```

```
516   "END";
517   "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
518   "BEGIN" "PRINT"(/L);
519   "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
520   "PRINT"SAMELINE,GAMMA[I,J];
521   "END";
522
523   "PRINT"(/L2S30)INITIAL BOND ORDERS ARE ALL ZERO);
524   K:=0,0;
525   "FOR"I:=1"STEP"1"UNTIL"ATOM NO-1"DO"
526   "FOR"J:=I+1"STEP"1"UNTIL"ATOM NO"DO"
527   "BEGIN"          BOI[I,J]:=0,0;
528   BOI[J,I]:=BOI[I,J];
529   K:=K+1;
530   BONDD[1,K]:=I;
531   BONDD[2,K]:=J;
532             "END";
533               "PRINT"(/L2);
534
535      "COMMENT" WE SET UP OUR INITIAL H,F; MATRIX ELEMENTS;
536            "FOR"J:=1"STEP"1"UNTIL"ATOM NO "DO"
537              "READ"Z[J];
538
539   "PRINT"(/L2S23)INITIAL HF MATRIX ELEMENTS);
540          "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
541   "BEGIN" SUMX:=0,0; N:=0,0;
542                 "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
543              "BEGIN""IF"J=I"THEN"
544                N:=0,5*P[I]*GAMMA[I,I]
545                "ELSE"
546                SUMX:=SUMX+(P[J]-Z[J])*GAMMA[I,J];
547              "END";
548            F[I,I]:=N+SUMX-VSIP[I];
549          "END";
550
551            "FOR"I:=1"STEP"1"UNTIL"ATOM NO-1"DO"
552            "FOR"J:=I+1"STEP"1"UNTIL"ATOM NO"DO"
553              "BEGIN"F[I,J]:=BETA[I,J]*0,5*BOI[I,J]*GAMMA[I,J];
554                     F[J,I]:=F[I,J];
555              "END";
556   "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
557   "BEGIN"     "PRINT"(/L);
558   "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
559   "PRINT"SAMELINE,F[I,J];
560   "END";
561
562   COUNT:=1;
563   EIGENSOLVE(F,SS,COEFF,ATOM NO,FAILED);
564   SORTOUT(COEFF,F,ATOM NO,MON,CC);
565   MCLACHLAN(ATOM NO,OCC,LAMBA,COEFF,MON);
566   PIPROPS(OCC,HINT,BONDD,COEFF,OCC,PI,ATOM NO,GAMMA,BETA,
567           Z,STORE,VSIP,COUNT);
568   "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
569   PII[I,COUNT]:=PI[I];
570          LOOP1: "PRINT"(/L);
571          COUNT:=COUNT+1;
572   "COMMENT" NOW WE SET OVERLAP INTEGRALS TO 1,0(I=J) OR 0,0 (I NE J)
573            AND WE SET UP VSIPS;
574        "FOR"I:=1"STEP"1"UNTIL"ATOM NO "DO"
```

TEXT
CUT OFF IN THE
ORIGINAL

```
576   "BEGIN"
577         "IF"J=I"THEN" SS[I,JJ]:=1,0 "ELSE" SS[I,JJ]:=0,0; FC[I,JJ]:=0,0;
578   "END";
579   QQ[1]:=1-2*XX[1]+PI[1];
580   QQ[2]:=XX[1]+XX[2]+XX[3]+PI[2]-4;
581   QQ[6]:=QQ[2];
582   QQ[3]:=XX[4]+XX[5]-XX[2]+PI[3]-2;
583   QQ[5]:=QQ[3];
584   QQ[4]:=XX[7]+XX[6]-XX[4]+PI[4]-2;
585   QQ[1]:=-QQ[1];
586   QQ[2]:=-QQ[2];
587   QQ[3]:=-QQ[3];
588   QQ[4]:=-QQ[4];
589   QQ[5]:=-QQ[5];
590   QQ[6]:=-QQ[6];
591
592   "COMMENT" NOW CALCULATE COULOMB REPULSION INTEGRALS;
593   "PRINT"(/"L2S9"ATOM"S10"VSIP");
594   "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
595   "BEGIN"
596   VSIP[I]:=11,230+4,967*QQ[I]+0,417*QQ[I]↑2;
597   VSIP[1]:=14,424+5,805*QQ[1]+0,413*QQ[1]↑2;
598   "PRINT"(/"L1S10",SAMELINE,/"S10",VSIP[I]);
599   "END";
600
601   "PRINT"(/"L2S25"1- AND 2-CENTRE COULOMB REPULSION INTEGRALS IN EV");
602   "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
603   "BEGIN"
604   GAMMA[I,I]:=15,894-1,153*(4-QQ[I]);
605   GAMMA[1,1]:=16,611-1,153*(5-QQ[1]);
606   "END";
607   "FOR"I:=1"STEP"1"UNTIL"ATOM NO-1"DO"
608   "FOR"J:=I+1"STEP"1"UNTIL"ATOM NO"DO"
609   "BEGIN"
610   AX[I,JJ]:=54,4/(GAMMA[I,I]+GAMMA[J,JJ]);
611   GAMMA[I,JJ]:=(1/(AX[I,JJ]*EXP((-RR[I,JJ]↑2)/(2*AX[I,JJ]↑2))+RR[I,JJ]))*27,2
612   GAMMA[J,I]:=GAMMA[I,JJ];
613   "END";
614   "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
615   "BEGIN" "PRINT"(/"L");
616   "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
617   "PRINT"SAMELINE,GAMMA[I,J]
618   "END";
619   "COMMENT" NOW CALCULATE DIAGONAL AND OFF-DIAGONAL ELEMENTS;
620   "PRINT"(/"L2S23"HF MATRIX ELEMENTS");
621      "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
622   "BEGIN" SUMX:=0,0; N:=0,0;
623                   "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
624                   "BEGIN""IF"J=I"THEN"
625                      N:=0,5*P[I]*GAMMA[I,I]
626                      "ELSE"
627                      SUMX:=SUMX+(P[J]-ZE[J])*GAMMA[I,JJ]
628                   "END";
629   FC[I,I]:=N+SUMX-VSIP[I];
630         "END";
631           "FOR"I:=1"STEP"1"UNTIL"ATOM NO-1"DO"
632           "FOR"J:=I+1"STEP"1"UNTIL"ATOM NO"DO"
633          "BEGIN"
634   FC[I,JJ]:=BETA[I,JJ]-0,5*BO[I,JJ]*GAMMA[I,JJ];
635   FC[J,I]:=FC[I,JJ];
```

```
636             "END";
637     "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
638     "BEGIN"     "PRINT"('L');
639     "FOR"J:=1"STEP"1"UNTIL"ATOM NO"DO"
640     "PRINT"SAMELINE,FCLI,JJ;
641     "END";
642     EIGENSOLVE(FC,SS,COEFF,ATOM NO,FAILED);
643     SORTOUT(COEFF,FC,ATOM NO,NON,CC);
644     MCLACHLAN(ATOM NO,OCC,LAMDA,COEFF,NON);
645     PIPROPS(OOC,NINT,BONDD,COEFF,OCC,PI,ATOM NO,GAMMA,BETA,
646             Z,STORE,VSIP,COUNT);
647     "FOR"I:=1"STEP"1"UNTIL"ATOM NO"DO"
648     "BEGIN"
649     PIICI,COUNT]:=PICI];
650     "IF"COUNT"GE"2"THEN"PICI]:=(PIICI,COUNT]+PIICI,COUNT-1])/2;
651     "END";
652
653     "COMMENT" TEST FOR CONVERGENCE OF TOTAL ENERGY IN ARRAY STORE,
654               GO TO LOOP1 IF TEST FAILS,OTHERWISE "FINISH";
655     "IF"COUNT<3"THEN""GOTO"LOOP1"ELSE""BEGIN"
656     "IF"ABS(STOREICOUNT]-STOREICOUNT-1])<.0-05"AND"ABS(STOREICOUNT]-STORE
657     ICOUNT-2])<.0-05"THEN""GOTO"FINISH;
658     "END";
659          "IF"COUNT=ITNO "THEN""GOTO"LABEL5 "ELSE""GOTO"LOOP1;
660
661       FAILED:"PRINT"('L2S10' AND YET THEIR REWARD APPEARETH NOT,');
662       "PRINT"('L2S10' AND THEIR LABOUR HATH NO FRUITE.....,');
663       "GOTO"LABEL5;
664       FINISH:"PRINT"('L2S20'ENERGY CONVERGED AFTER',COUNT,'ITERATIONS');
665       LABEL5:"PRINT"('L6S20'SUMMARY OF TOTAL ENERGY CALCULATIONS');
666       "PRINT"('L3S15'ITERATION NO,'S10',TOTAL ENERGY');
667       "FOR"I:=1"STEP"1"UNTIL"ITNO"DO"
668       "PRINT"('L2S20'',I,('S10''),STOREII];
669       "END";
670     "END";
671     "END";
 1178     MC
 6880  CODE
 8058 TOTAL


 &END;
CPU TIME =  0000  55,600  REAL TIME   00 01 27
   A
```

REFERENCES

1. P.A.M. Dirac: Proc. Roy. Soc. (Lond) A123 714 (1929)
2. B.J. Duke: Annual Reports on the Progress of Chemistry 68 3 (1971)
3. P.G. Lykos: Advances in Quantum Chemistry 1 171 (1964)
4. For example, K. Jug: Theoret Chim. Acta 14 91 (1969)
5. M.A. Whitehead: personal communication to the author.
6. L. Pauling, E.B. Wilson: "Introduction to Quantum Mechanics" (McGraw - Hill, 1935) P.259.
7. C.C.J. Roothaan: Rev. Mod. Phys. 23 69 (1951)
8. a. W. Moffitt: Proc. Royal Soc. (Lond) A210 327 (1952)
   b. O. Sinanoglu: Proc. Nath. Acad. Sci. 47 1217 (1961)
9. For example, J.D. Roberts: "Notes on Molecular Orbital Calculations" (W.A. Benjamin, New York, 1962)
10. a. R. Daudel: "The Fundamentals of Theoretical Chemistry" (Pergamon Press, 1968)
    b. K. Fukui: in "Modern Quantum Chemistry. Part I. Orbitals" ed. O. Sinanoglu (Academic Press, 1965) P.49.
11. R. Parr: "Quantum Theory of Molecular Electronic Structure" (W.A. Benjamin, 1963) P.7.
12. S.F. Boys: Proc. Roy. Soc. (Lond) A200 542 (1950)
13. R.E. Christoffersen: Advances in Quantum Chemistry 6 333 (1972)
14. W.J. Hehre, R.F. Stewart, J.A. Pople: J. Chem. Phys. 51 2657 (1969)
15. a. A.A. Frost: J. Chem. Phys. 47 3707 (1967)
    b. S.Y. Chu, A.A. Frost: J. Chem. Phys. 54 764 (1971)
16. For example, M. Kasha: J. Chim. Phys. 58 914 (1961)
17. A.E. Hansen: Theoret. Chim. Acta 7 230 (1967)
18. R. Pariser: J. Chem. Phys. 21 568 (1953)
19. For example, J.S. Kwiatowski: Theoret. Chim. Acta 10 47 (1968)
20. M. Kaplansky, M.A. Whitehead: Mol. Phys. 15 149 (1968)
21. G. Herzberg, J. Shoosmith: Canad. J. Phys. 34 523 (1956)

22. a. D.H. Lo, M.A. Whitehead: J. Chem. Soc. A1463 (1971)
b. I. Fischer - Hjalmars: Arkiv. Fysik 21 123 (1962)

23. G.D. Zeiss, M.A. Whitehead: J. Chem. Soc.A 1727 (1971)

24. E. Lindholm, C. Frich, L. Asbrink: Faraday Discussion 54 at Sussex University, September 1972.

25. K. Nishimoto, L.S. Forster: Theoret. Chim. Acta 4 155 (1966)

26. A.R. Buick, T.J. Kemp, G.T. Neal, T.J. Stone: J. Chem. Soc.A1609 (1969)

27. M.J.S. Dewar, E. Haselbach: J. Amer. Chem. Soc. 92 590 (1970)

28. R. Daudel: Advances in Quantum Chemistry 1 115 (1964)

29. R. Daudel, R. Lefebvre, C. Moser: "Quantum Chemistry" (Interscience 1961)

30. T.E. Peacock: "Electronic Properties of Aromatic and Heterocyclic Molecules" (Academic Press, 1965) P.91.

31. K. Ruedenberg: ibid Ref.10b P.85.

32. a. C. Edriston, K. Ruedenberg: J. Chem. Phys. 43 S.97 (1965)
b. W. von Niessen: Theoret. Chim. Acta 29 29 (1973)

33. D. Peters: J. Chem. Soc. 4017 (1963)

34. D. Peters: Tetrahedron 19 143 (1963)

35. C.A. Coulson: "Valence" (Oxford University Press, 1965) P.174

36. C.A. Coulson, H.C. Longuet-Higgins: Proc. Roy. Soc. (Lond.) A 191 39 (1947)

37. a. R. Daudel, R. Lefebvre, C. Moser: ibid. Ref.29 P.91.
b. G.G. Hall: Proc. Roy. Soc. (Lond) A205 541 (1951)

38. H. Hamano: Bull. Chem. Soc. Jap. 37 1574 (1964)

39. J.M. Parks, R.G. Parr: J. Chem. Phys. 28 335 (1958)

40. K. Sundamm: Chem. Phys. Letters 13 292 (1970)

41. D.A. Evans: M. Sc. Thesis P.36

42. a.J. Hinze, M.A. Whitehead, H.H. Jaffe: J. Amer. Chem. Soc. 85 148 (1963)
b. M.A. Whitehead, N.C. Baird, H. Kaplansky: Theoret. Chim. Acta.3 135 (1965)

43. H.D.B. Jenkins: Unpublished work.

44. D.A. Evans: ibid Ref.41 P.21.

45. G. Del Re: J. Chem. Soc. 4031 (1958)

46. G. Del Re: in "Electronic Aspects of Biochemistry" ed. B Pullman (Academic Press, 1964)

47. K. Ghosh, G. Bhattacharyya, P. Sen: Int. J. Quant. Chem. 4 347 (1970)

48. G. Bhattacharyya, A. Bhaumik: Int. J. Quant. Chem. 6 935 (1972)

49. R.S. Mulliken: J. Chem. Phys. 46 539 (1949)

50. R. Hoffmann: J. Chem. Phys. 39 1397 (1963)

51. N.C. Baird, J.M. Sichel, M.A. Whitehead: Theoret. Chim Acta. 11 38 (1968)

52. G. Koyrin: J. Amer. Chem. Soc. 86 1463 (1964), ibid 4550 (1964) ibid 87 3300 (1965)

53. W. Moffitt: Proc. Roy. Soc. (Lond) A196 510 (1949)

54. L.C. Cusachs, J.W. Reynolds: J. Chem. Phys. 43 S.160 (1965)

55. R. Ferreira: Advances in Chemical Physics 13 55 (1967)

56. J.K. Bates, R. Ferreira: Theoret Chim. Acta. 16 111 (1970)

57. H.D.B. Jenkins, J.B. Pedley: Theoret. Chem. Acta 3 309 (1965)

58. D. Tong: Personal communication to H.D.B. Jenkins.

59. J.A. Pople: Trans. Faraday Soc. 49 1375 (1953)

60. D.A. Evans: ibid Ref.41 P.140

61. J.M. Sichel, M.A. Whitehead: Theoret Chim. Acta. 5 35 (1966)

62. H. J. Silverstone, H.W. Joy: J. Chem. Phys. 47 1384 (1966)

63. C.H. Townes, B.P. Dailey: J. Chem. Phys. 23 118 (1959)

64. D.A. Evans: ibid Ref. 41 P.113

65. D. Zerolm: Chem Phys. Letters 14 471 (1972)

66. H. Siegbahn, K. Siegbahn: Uppsala University Institute of Physics publication UUIP 823 (1973)

67. T.D. Thomas: J. Amer. Chem. Soc. 92 4184 (1970)

68. M.E. Schwarz: Chem Phys. Letters 6 631 (1971)

69. T.G. Edwards: Theoret. Chim. Acta 27 1 (1972)

70. K. Siegbahn: Uppsala University Institute of Physics publication UUIP 793 (1972)

71. T.A. Carlson: in "Electron Spectroscopy" ed. D.A. Shirley (North Holland Publishing Co., Amsterdam, 1972)

72. U.E. Schwarz: ibid P.605

73. K. Siegbahn: ibid P.16

74. P.A. Cox, S. Evans, A.F. Orchard. N.V. Richardson, P.J. Roberts: Faraday Discussion 54 at Sussex University, September 1972.

75. K. Siegbahn, D. Hammond, H. Fellner-Feldegg, E.F. Barnett: Science 176 245 (1972)

76. W.L. Jolly: Faraday Discussion 54 at Sussex University, September 1972.

77. H. Basch, L.C. Snyder: Chem. Phys. Letters 3 333 (1969)

78. For example, L. Salem: "M.O. Theory of Conjugated Systems" (Benjamin, New York, 1966)

79. C. Sandorfy: Canad. J. Chem. 33 1337 (1955)

80. K. Fukui, H. Kata, T. Yonezawa: Bull. Chem. Soc. Jap. 33 1197 1201 (1960)

81. K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura, C. Nagata: Bull. Chem. Soc. Jap. 35 38 (1962)

82. K. Fukui, H. Kato, T. Yonezawa: Bull. Chem. Soc. Jap. 34 3,443 (1961)

83. S. Katagiri, C. Sandorfy: Theoret Chim. Acta. 4 203 (1966)

84. R. Pariser, R.G. Parr: J. Chem. Phys. 21 466, 767 (1953)

85. L.B. Kier: Tetrahedron Letters 3272 (1965)

86. R.D. Brown, M.L. Hefferman: Austral. J. Chem. 12 319, 330, 543, 554 (1959)

87. R.D. Brown, M.L. Hefferman: Austral. J. Chem. 13 38 (1960)

88. R.D. Brown, B.A.W. Collar, M.L. Hefferman: Tetrahedron 18 343 (1962)

89. F. Monicchioli, G. Del Re: J Chem. Soc. B 674 (1969)

90. C.T. Yim, M.A. Whitehead, D.H. Lo; Canad. J. Chem. 46 3595 (1968)

91. R.M. Hart, M.A. Whitehead: Trans. Faraday Soc. 67 1509 (1971)

92. L.Krause, M.A. Whitehead: J. Chem. Soc. B. 2433 (1971)

93. a.J.A. Pople, D.P. Santry, G.A. Segal: J. Chem. Phys. 43 S.129 (1965)
b.J.A. Pople, G.A. Segal: J. Chem. Phys. 43 S.136 (1965)

94. J.A. Pople, D.L. Beveridge, P.A. Dobosh: J. Chem. Phys. 47 2026 (1967)

95. a.E. Clementi: J. Chem. Phys. 46 4731 (1967)
b.R.G. Body, D.S. McClure: J. Chem. Phys. 48 4916 (1968)

96. W.J. Hehre, R. Ditchfield, L. Radom, J.A. Pople: J. Amer. Chem. Soc. 92 4796 (1970)

97. D.A. Evans: ibid Ref. 41 P.55

98. A. Streitwieser, Jr: "Molecular Orbital Theory for Organic Chemists" (Wiley, New York, 1961)

99. L.B. Kier: "Molecular Orbital Theory in Drug Research" (Academic Press, 1971)

100. A. Pullman, B. Pullman: "Quantum Biochemistry" (Interscience, John Wiley and Sons, 1963)

101. M. Scholz, D. Heidrich: Monatsch 98 254 (1967)

102. N.C. Baird, M.A. Whitehead: Canad. J. Chem. 44 1933 (1966)

103. R.D. Brown, B.A.W. Coller: Theoret Chim. Acta 7 259 (1967)

104. J.T. Gleghorn: J. Chem. Soc. Perk. Trans. 2 479 (1972)

105. D.T. Clark: Tetrahedron 24 4689 (1968)

106. P.J. Black, R.D. Brown, M.L. Heffernan: Austral. J. Chem. 20 1325 (1967)

107. E. Clementi, H. Clementi, D.R. Davis: J. Chem. Phys. 46 4725 (1967)

108. H. Solony, F.W. Birss, J.B. Greenshields: Canad. J. Chem. 43 1569 (1965)

109. P.J. Black, R.D. Brown, M.L. Heffernan: Austral J. Chem. 20 1305 (1967)

110. T.B. Cobb, J.D. Memety: J. Chem. Phys. 50 4262 (1969)

111. T.E. Peacock: J. Chem. Phys. 21 767 (1965)

112. K. Nishimoto, L.S. Forster: Theoret. Chim. Acta. 4 155 (1966)

113. N.C. Baird, M.J.S. Dewar, R. Sustman: J. Chem. Phys. 50 1275 (1969)

114. D.T. Clark: Tetrahedron 24 3285 (1968)

115. C.A. Coulson, ibid Ref.35 P.195.

116. A.L. McClellan: "Tables of Experimental Dipole Moments" (W.H. Freeman and Co., San. Francisco, 1963)

117. R. Rhoauley, L.A. Burnelle, C. Sandorfy: Theoret. Chim. Acta. 22 1 (1973)

118. D.L. Dowmidge, J. Hinze: J. Amer. Chem. Soc. 93 3107 (1971)

119. R.D. Brown, M.L. Heffernan: Trans. Faraday. Soc. 54 757 (1958)

120. J.N. Ensley: J. Chem. Soc. A.2523 (1968)

121. B. Edlen: J. Chem. Phys. 33 98 (1960)

122. L. Paolini: Nuovo Cimento 4 410 (1956)

123. L.E. Sutton: "Tables of Interatomic Distances and Configurations in Molecules and Ions" (Chem. Soc. Special Publication 1958)

124. T. Koopmans: Physica 1 104 (1934)

125. H.I. Al-Jobory, D.W. Turner: J. Chem. Soc. 4434 (1964)

126. J. Omura, K. Higasi, H. Baba: Bull. Chem. Soc. Jap. 29 501, 521 (1956)

127. D.W. Turner: Adv. Phys. Org. Chem. 4 31 (1966)

128. A.J. Yencha, N.A. El-Sajad: J. Chem. Phys. 48 3469 (1968)

129. M.J.S. Dewar, S.D. Worley: J. Chem. Phys. 50 654 (1969)

130. D. Cook: J. Amer. Chem. Soc. 80 49 (1958)

131. T.W. Sugden, A.D. Walsh, W.C. Price: Nature 148 372 (1941)

132. J.D. Morrison, R.W. Wood: J. Chem. Phys. 3 439 (1935)

133. P. Lindner, R. Manne, I. Hartensson: Theoret Chim Acta 5 406 (1966)

134. N.C. Baird, M.J.S. Dewar, R. Sustman: J. Chem. Phys. 50 1275 (1969)

135. W.G. Richards, J.A. Horsley: "Ab initio' Molecular Orbital Calculations for Chemists" (Clarendon Press, Oxford. 1970)

136. R.L. Flurry, W. Stout, J.J. Bell: Theoret Chim. Acta. 8 203 (1967)

137. K. Nishimoto, L.S. Forster: Theoret. Chim. Acta. 4 155 (1966)

138. L.C. Cusachs. P. Politzer: Chem. Phys. Letters 1 529 (1968)

139. P-O Lowdin: J. Chem. Phys. 18 365 (1950)

140. P. Politzer, R.S. Mulliken: J. Chem. Phys. 55 5135 (1971)

141. a. P. Politzer; Theoret. Chem. Acta. 23 203 (1971)
b. P. Politzer, E.W. Stout, Jr.: Chem. Phys. Letters 8 519 (1971)
c. P. Politzer, R.R. Harris: J. Amer. Chem. Soc. 92 6451 (1970)

142. N.L. Bailey, M.P.L. Bailey: Theoret. Chim. Acta. 16 303 (1970)

143. W.J. Hehre, R.F. Stewart, J.A. Pople: FaradaySymposium (1968)

144. J.A. Pople, D.L. Beveridge: "Approximate Molecular Orbital Theory" (McGraw-Hill, 1970)

145. K.F. Freed: Chemical Physics Letters 13 181 (1972)

146. J. Thorhallson, C. Fisk, S. Fraga: Theoret. Chim. Acta 12 80 (1968)